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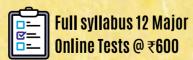
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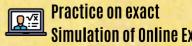




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#### **Managing Editor**

Mahabir Singh

Editor

Anil Ahlawat

#### **Corporate Office:**

Plot 99, Sector 44 Institutional area, Gurgaon -122 003 (HR). Tel: 0124-6601200 e-mail: info@mtg.in website: www.mtg.in

406, Taj Apartment, Near Safdarjung Hospital, New Delhi - 110029.

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# NEET JEE ESSENTIALS

Class XI



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Unit 6

The p-Block Elements (Group 13 and 14)

#### **GROUP-13 ELEMENTS (BORON FAMILY)**

#### Introduction

Group-13 of the periodic table consist of the following elements with general configuration  $ns^2np^1$ . A new element is added to group-13 *i.e.*, nihonium (Nh), which is radioactive.

Element	Electronic configuration
B (5)	[He] $2s^2 2p^1$
Al (13)	[Ne] $3s^2 3p^1$
Ga (31)	[Ar] $3d^{10} 4s^2 4p^1$
In (49)	$[Kr] 4d^{10} 5s^2 5p^1$
Tl (81)	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$
Nh (113)	[Rn] $5f^{14} 6d^{10} 7s^2 7p^1$

#### **Physical Properties**

#### Atomic and ionic radii

• The atomic/ionic radius increases from B to Tl (exception Al > Ga).

#### Ionisation energy

*I.E.* decreases down the group. Successive *I.E.* increases in the order :

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$$

#### Electronegativity

Boron has the maximum electronegativity among the group-13 elements. Electronegativity first decreases from B to Al and then increases down the group.

#### Metallic character

B is a non-metal while Al is a metal and all other elements are almost metallic in character.

#### **Density**

As we move down the group, density increases.

#### Boiling point .....

Boiling points of group-13 elements follow a regular trend and decreases down the group.

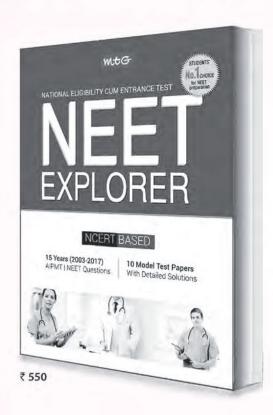
#### Melting point .....

The melting points decreases from B to Ga and then increases from Ga to Tl.

The melting point of boron is very high because it has giant covalent polymer structure in both solid and liquid states.



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#### **Oxidation states**

B and Al show +3 oxidation states only but Ga, In and Tl show +1 and +3 oxidation states due to inert pair effect.

#### Inert pair effect

The two *s*-electrons in the outer shell tend to remain paired and will not participate in compound formation. This effect is called inert pair effect. The inert pair effect increases gradually in Ga, In and Tl compounds e.g., Ga<sup>+</sup> compounds are unstable, In compounds are moderately stable, whereas Tl compounds are most stable.

#### Reactivity towards air

- $4M_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2M_2O_{3(s)}$ (M = B, Al, Ga, In, Tl)
- $2M_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2MN_{(s)}$ (M = B, Al)
- On moving down the group, the acidic character of oxides decreases and the basic character increases.

#### Reactivity towards water

- Boron is not affected by water or steam. Red hot boron decomposes steam.  $2B + 3H_2O \longrightarrow B_2O_3 + 3H_2$
- Aluminium can decompose the steam.  $2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$
- Ga and In are attacked by water only in the presence of oxygen.
- Tl is attacked by moist air.  $4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$

#### Chemical Properties

#### Reactivity towards acids and alkalies

Boron does not react with non-oxidising acids while others react with acids e.g.,

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al_{(aq)}^{3+} + 6Cl_{(aq)}^{-} + 3H_{2(g)}$$

- Conc. HNO<sub>3</sub> makes Al passive due to the formation of thin layer of Al<sub>2</sub>O<sub>3</sub>.
- Boron resist the action of alkalies upto 773 K.  $2B_{(s)} + 6KOH_{(aq)} \xrightarrow{> 773 \text{ K}} 2K_3BO_{3(s)} + 3H_{2(q)}$
- Al and Ga being amphoteric also react with aqueous alkalies.

$$2M_{(s)} + 2\text{NaOH}_{(aq)} + 6\text{H}_2\text{O}_{(l)} \longrightarrow 2\text{Na}^+[M(\text{OH})_4]_{(aq)}^- + 3\text{H}_{2(g)}$$
 $(M = \text{Al, Ga})$ 

#### **Reactivity towards non-metals**

At high temperature, B reacts directly with all non-metals except H, Ge, Te and the noble gases.

$$4B + C \xrightarrow{\Delta} B_4C$$

$$4B + 3O_2 \xrightarrow{\Delta} 2B_2O_3$$

$$2B + 3S \xrightarrow{\Delta} B_2S_3$$

Al combines with most of the non-metals on heating.

### Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI<sub>3</sub>).

$$2M_{(s)} + 3X_{2(g)} \longrightarrow 2MX_{3(s)}$$
 (X = F, Cl, Br, I)

Lewis acid character decreases down the group  $BX_3 > AlX_3 > GaX_3 > InX_3$ 

(Due to increase in size)

Lewis acid character of boron trihalides  $BI_3 > BBr_3 > BCl_3 > BF_3$ 

(Due to  $p\pi$ - $p\pi$  back bonding)



#### Turning dirty aluminium foil into biofuel catalyst!

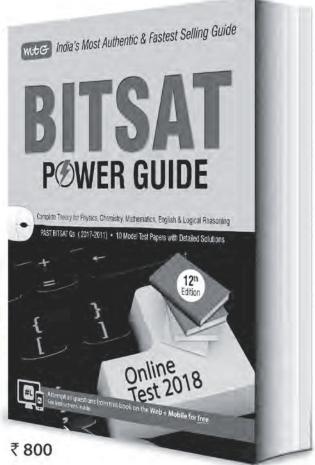
Recently, an innovative crystallization method is developed to obtain 100% pure single crystals of aluminium salts from the contaminated foil. This is the starting material for the preparation of alumina catalyst. Usually to produce this type of alumina it would have to come from bauxite ore, which in mined in countries such as West Africa, West Indies and Australia, causing huge environmental damage.



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#### Anomalous Behaviour of Boron

Boron shows anomalous behaviour as compared to the other members of the group due to

- its smallest size and high ionization energy
- highest electronegativity
- absence of *d*-orbitals in its valence shell.

#### **Points of Differences**

- B forms only covalent compounds while others form both ionic and covalent compounds.
- Trihalides of B are monomeric while other elements have halogen bridged dimeric structures.
- B has two allotropic forms; crystalline and amorphous. Other members do not show allotropy.
- The melting and boiling points of B are much higher as compared to other members.

 Boron shows a maximum covalency of four in its compounds e.g., BH<sub>4</sub> while other members show a maximum covalency of six e.g., [AlF<sub>6</sub>]<sup>3-</sup>.

#### Uses

#### **Aluminium**

- It forms many useful alloys with Cu, Mn, Mg, Si and Zn.
- It is used as a conductor for transmission of electricity.
- It is used for making silvery paints for covering iron or other materials.

#### **Boron**

- As a moderator in nuclear reactors.
- As an abrasive and a refractory material.
- As rocket fuels because of high energy/mass ratio.
- As a hardener in steel industry.

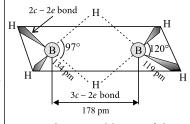
#### IMPORTANT COMPOUNDS OF BORON AND ALUMINIUM

	Preparation	Properties	Structure
$\begin{array}{c} \text{Borax} \\ \text{(Na}_2 \text{B}_4 \text{O}_7.10 \text{H}_2 \text{O}) \end{array}$	Colemanite Borax $+ 2NaBO_2 + 2CaCO_3 \downarrow$ $4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7$ $+ Na_2CO_3$	$Na_{2}B_{4}O_{7}\cdot 10H_{2}O \xrightarrow{\Delta} Na_{2}B_{4}O_{7} + 10H_{2}O$ $Na_{2}B_{4}O_{7} \xrightarrow{\Delta} 2NaBO_{2} + B_{2}O_{3}$ $Transparent glassy bead$ $Na_{2}B_{4}O_{7} + 2NaOH \longrightarrow 4NaBO_{2} + H_{2}O$ $Na_{2}B_{4}O_{7} + H_{2}SO_{4} \longrightarrow Na_{2}SO_{4}$ $+ H_{2}B_{4}O_{7}$	$2Na^{+} \begin{bmatrix} OH \\ B^{-} \\ OO \\ B - OH \\ OH \end{bmatrix}$ $Na_{2}[B_{4}O_{5}(OH)_{4}] \cdot 8H_{2}O$
	Uses: <ul><li>As a water softener and a clean</li><li>In the laboratory for borax bea</li></ul>	0 0	
Orthoboric acid (H <sub>3</sub> BO <sub>3</sub> )	$Na_{2}B_{4}O_{7} + 2HCl + 5H_{2}O \longrightarrow 4H_{3}BO_{3} + 2NaCl$ $Na_{2}B_{4}O_{7} + H_{2}SO_{4} + 5H_{2}O \longrightarrow 4H_{3}BO_{3} + Na_{2}SO_{4}$ $Ca_{2}B_{6}O_{11} + 4SO_{2} + 11H_{2}O \longrightarrow 2Ca(HSO_{3})_{2} + 6H_{3}BO_{3}$ $B_{2}H_{6} + 6H_{2}O \longrightarrow 2H_{3}BO_{3} + 6H_{2}$ $BN + 3H_{2}O \longrightarrow H_{3}BO_{3} + NH_{3}$	$H-OH + B(OH)_{3} \longrightarrow [B(OH)_{4}]^{-} + H^{+};$ $pK_{a} = 9.25$ $H_{3}BO_{3} \xrightarrow{370 \text{ K}} HBO_{2} + H_{2}O$ $\downarrow^{410 \text{ K}}_{-H_{2}O} H_{2}B_{4}O_{7}$ $\downarrow^{\text{Red Hot}}_{2B_{2}O_{3} + H_{2}O}$ $B(OH)_{3} + 3C_{2}H_{5}OH \xrightarrow{\text{Conc. } H_{2}SO_{4}}_{B(OC_{2}H_{5})_{3} + 3H_{2}O}$	H B H H O O O O O O O O O O O O O O O O

#### Uses:

- It is used in the manufacture of heat resistant borosilicate glass.
- The aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the name boric lotion.

$$\begin{array}{c} 2 \text{NaBH}_4 + \text{I}_2 \xrightarrow{\text{Diglyme}} \Rightarrow \text{B}_2 \text{H}_6 \\ + 2 \text{NaI} + \text{H}_2 \\ 2 \text{BF}_3 + 6 \text{NaH} \xrightarrow{450 \text{ K}} \Rightarrow \text{B}_2 \text{H}_6 + \\ 6 \text{NaF} \\ 4 \text{BF}_3.\text{Et}_2 \text{O} + 3 \text{LiAlH}_4 \xrightarrow{\text{Diethyl}} \Rightarrow \\ 2 \text{B}_2 \text{H}_6 + 3 \text{LiF} + 3 \text{AlF}_3 + 4 \text{Et}_2 \text{O} \\ \end{array} \begin{array}{c} \text{B}_2 \text{H}_6 + 3 \text{O}_2 \longrightarrow \text{B}_2 \text{O}_3 + 3 \text{H}_2 \text{O};} \\ \Delta_c H^\circ = -1976 \text{ kJ mol}^{-1} \\ \text{B}_2 \text{H}_6 + 6 \text{H}_2 \text{O} \longrightarrow 2 \text{H}_3 \text{BO}_3 + 6 \text{H}_2 \\ \text{B}_2 \text{H}_6 + 6 \text{CH}_3 \text{OH} \longrightarrow 2 \text{B(OCH}_3)_3 + 6 \text{H}_2 \\ \text{B}_2 \text{H}_6 + 2 \text{NMe}_3 \longrightarrow 2 \text{BH}_3 \cdot \text{NMe}_3 \\ 3 \text{B}_2 \text{H}_6 + 6 \text{NH}_3 \xrightarrow{\text{Low temp.}} \Rightarrow \\ 3 \text{[BH}_2 (\text{NH}_3)_2]^+ \text{[BH}_4]^- \xrightarrow{473 \text{ K}} \Rightarrow \\ 2 \text{B}_3 \text{N}_3 \text{H}_6 + 12 \text{H}_2 \\ \end{array}$$



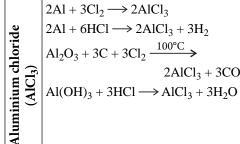
Due to the resemblance of three centre two electron bond to a banana, it is also called banana bond.

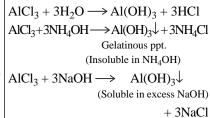
#### Uses:

For preparing a number of borohydrides reducing agent such as LiBH<sub>4</sub>, NaBH<sub>4</sub>, etc, in organic reaction.

 $2B_3N_3H_6 + 12H_2$ 

To make bullet-proof vests and light composite material for aircrafts.





Gelatinous ppt.

(Insoluble in 
$$NH_4OH$$
)

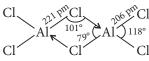
Al $Cl_3 + 3NaOH \longrightarrow Al(OH)_3 \downarrow$ 

(Soluble in excess  $NaOH$ )

 $+ 3NaCl$ 

Al $(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$ 

(Soluble meta-aluminate)



(Tetrahedral) AlCl<sub>3</sub> achieves stability by forming dimer.

#### Uses:

- Anhydrous AlCl<sub>3</sub> is used as a catalyst in Friedel-Crafts reaction and in cracking of petroleum.
- It is extensively used in manufacture of dyes, drugs and perfumes.

### GROUP-14 ELEMENTS (CARBON FAMILY)

#### Introduction

Group-14 is transition between metals and non-metals. C is the most versatile element. Organic chemistry is devoted to carbon containing compounds. A new element is added to group-14, i.e., Flerovium (Fl) which is radioactive.

Group-14 contains the following elements with general electronic configuration  $ns^2 np^2$ .

Element	Electronic configuration
Carbon (6)	[He] $2s^2 2p^2$
Silicon (14)	[Ne] $3s^2 3p^2$
Germanium (32)	[Ar] $3d^{10} 4s^2 4p^2$
Tin (50)	[Kr] $4d^{10} 5s^2 5p^2$
Lead (82)	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
Flerovium (114)	[Rn] $5f^{14} 6d^{10} 7s^2 7p^2$

#### **Physical Properties**

#### **Covalent and ionic radii**

Covalent radii of group-14 elements regularly increases with increase in atomic number. The same trend is observed with ionic radius in their +2 and +4 oxidation states.

#### **Ionisation energy**

First I.E. decreases from C to Sn but the decrease is not regular, decrease is very sharp from C to Si, but from Si onwards the decrease is very little due to poor shielding effect of 3d- and 4d- electrons in Ge and Sn. Pb is having a little more I.E. than Sn but less than Ge due to lanthanide contraction. Thus, the first I.E. of group-14 elements follow the order: C > Si > Ge > Sn < Pb

#### **Electronegativity**

C is the most electronegative element in this group. Electronegativity decreases from C to Si and remain constant from Si to Sn and then slightly increases for Pb.

#### **Density**

C (diamond) has more density than Si. Except carbon, the density of group-14 element increases with increase in atomic number.

#### Melting point and boiling point

The m.pt. and b.pt. decreases as we move down the group due to corresponding decrease in the interatomic forces of attraction. However, exceptionally the m.pt. of Sn is lower than that of Pb.

The m.pt. and b.pt. of group-14 elements are higher than the corresponding group-13 elements due to the formation of four covalent bonds with each other resulting in strong binding forces between their atoms in solid as well as in liquid state.

#### Metallic and non-metallic character

Metallic character increases with increase in atomic number.

C Si Ge Sn Pb Non-metal Metalloid Wetal



#### Carbon Nanotube Hybrid Structure!

To introduce and control the temperature coefficient of resistance (TCR) of metal matrix composite, relatively thick and short multi-walled carbon nanotubes (MWCNTs) were introduced in the metal matrix with in-situ formation of chromium carbide (Cr<sub>7</sub>C<sub>3</sub>) at the CNT/copper (Cu) interface. Incompatible properties such as electrical conductivity and TCR can be achieved simultaneously by introducing MWCNTs in the Cu matrix, with control of the interfacial resistivity using the MWCNT/Cr<sub>7</sub>C<sub>3</sub>-Cu system.

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#### **Chemical Properties**

#### **Oxidation states**

C and Si both show an oxidation state of +4 while all other elements of group-14 show two oxidation states of +2 and +4 due to inert pair effect. The stability of +2 oxidation state 2+ 2+ 2+ increases from Ge to Pb *i.e.*, Ge < Sn < Pb, while the stability of +4 oxidation state decreases from 4+ 4+ 4+ 4+ 4+ 4+ C to Pb *i.e.*, C > Si > Ge > Sn > Pb

#### Oxidising and reducing properties

- Order of the reduction power in +2 oxidation state:
   C > Si > Ge > Sn > Pb
- Order of oxidation power in +4 oxidation state :
   C < Si < Ge < Sn < Pb</li>

#### Reactivity towards oxygen

- They form oxides when heated in oxygen but do not react with oxygen at ordinary temperature.
- Group-14 elements form monoxides (MO) and dioxides (MO<sub>2</sub>). SiO exists only at high temperature.
- Acidic nature of oxides:

$$\begin{array}{c|ccccc} CO_2 & SiO_2 & GeO_2 \\ \hline & Acidic & & Amphoteric \\ \hline CO & GeO & SnO & PbO \\ Neutral & Acidic & & Amphoteric \\ \end{array} \qquad \begin{array}{c} SnO_2 & PbO_2 \\ \hline & Amphoteric \\ \end{array} \qquad \begin{array}{c} (MO_2 \text{ type}) \\ \hline & (MO \text{ type}) \\ \hline \end{array}$$

Pb can from Pb<sub>3</sub>O<sub>4</sub> (trilead tetraoxide), known as red lead or sindhur, on heating PbO (litharge) with excess of air at 673 K.  $6\text{PbO} + \text{O}_3 \frac{673 \text{ K}}{2} 2\text{Pb}_3\text{O}_4$ 

#### Anomalous Behaviour of Carbon

C differs from the rest of the members of group-14 because of

- its small atomic size
- its high electronegativity
- its property of catenation
- absence of *d*-orbitals in its valence shell.

#### **Points of Differences**

• The m.pt. and b.pt., *I.E.* and electronegativity of C is very high as compared to the other members of its family.

#### Reactivity towards water

• C, Si and Ge are not affected by water. Sn decomposes steam.

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

- Pb is unaffected by water on its surface probably because of a protective oxide film formation.
- Pb dissolved slowly in water containing dissolved oxygen. This is called plumbosolvency.
   2Pb + 2H<sub>2</sub>O + O<sub>2</sub> → 2Pb(OH)<sub>2</sub>

#### Reactivity towards halogen

- These elements can form halides of formula  $MX_2$  and  $MX_4$  (X = F, Cl, Br, I).
- Except carbon, all other members react directly with halogen.
- Stability of dihalides increases down the group.
- Except CCl<sub>4</sub>, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in vacant d-orbitals.

#### **Reducing character**

• Carbon is a powerful reducing agent, it can reduces oxides of various elements *e.g.*,

$$SnO_2 + 2C \xrightarrow{\Delta} Sn + 2CO$$
  
 $CO_2 + C \xrightarrow{\Delta} 2CO$   
 $Fe_2O_3 + 3CO \xrightarrow{250^{\circ} -700^{\circ}C} 2Fe + 3CO_2$ 

- Si is also used as deoxidizer in the manufacture of steel in the form of ferrosilicon.
- Sn also acts as a good reducing agent.
- Carbon in its diamond form, is one of the hardest known element.
- It has maximum tendency to show catenation.
- Carbon has strong tendency to form pπ-pπ multiple bonds either with itself or with other elements like N, O, S, etc. Other members of the family form pπ-dπ bonds and that to a lesser extent.
- CO<sub>2</sub> is a gas while the dioxides of all other members are solids.
- Carbon shows a maximum covalency of four while other members of the family may expand their covalency beyond 4 *e.g.*, [SiCl<sub>6</sub>]<sup>2-</sup>.

#### ALLOTROPES OF CARBON

- **Diamond :** In diamond, C-atom is  $sp^3$  hybridised and has three dimensional network structure. Since, no free electron is available, it is a bad conductor of electricity.
- **Graphite:** C-atom is  $sp^2$  hybridised and each carbon is directly bound to three other C-atoms. Thus, graphite has a delocalized  $\pi$ -electron cloud, which is responsible for its high electrical conductivity. It possesses layer structure.
- Fullerenes: It consists 12 pentagons and 20 hexagons folded into a sphere, so that it looks like a soccer ball, called 'bucky ball'.

All the carbon atoms are equal and they undergo  $sp^2$  hybridisation.

#### USES OF CARBON

- Graphite is used as a lubricant, electrodes for dry cell, moderator for fast moving neutrons in nuclear reactor.
- Graphite is used in lead pencils.
- Diamond is used for cutting glass and other cutting and drilling tools. It is also used for making precious gems and jewellery.
- Being highly porous, activated charcoal is used in adsorbing poisonous gases, also used in water filters to remove organic contaminators and in air conditioning system to control odour.

#### IMPORTANT COMPOUNDS OF CARBON AND SILICON

	Preparation	Properties	Structure
Carbon	$2C + O_2 \xrightarrow{\Delta} 2CO$	$2CO + O_2 \longrightarrow 2CO_2$	:C=Q: <b>←→</b> _:C≡Q:
monoxide	$HCOOH \xrightarrow{373 \text{ K}} H_2O$	$3\text{CO} + \text{Fe}_2\text{O}_3 \xrightarrow{\Delta} 2\text{Fe} + 3\text{CO}_2$	or :C≌O:
(CO)	$\begin{array}{c} 2C + O_2 \xrightarrow{\longrightarrow} 2CO \\ HCOOH \xrightarrow{373 \text{ K}} Conc. H_2SO_4 & + CO \\ C + H & O & 473 - 1273 \text{ K} \end{array}$	$CO + ZnO \xrightarrow{\Delta} Zn + CO_2$	(Linear structure with
	$C + H_2O \xrightarrow{473 - 1273 \text{ K}}$		<i>sp</i> hybridisation)
	$^{2}$ CO+H <sub>2</sub>	$5\text{CO} + \text{Fe} \xrightarrow{180^{\circ}\text{C}} [\text{Fe}(\text{CO})_5]$	
	Water gas	CO is highly poisonous gas as it forms a	
	$2C + O_2 + 4N_2 \xrightarrow{473 - 1273 \text{ K}}$	complex with haemoglobin (Hb) which is	
	$2C + O_2 + 4N_2 \longrightarrow 2CO + 4N_2$	$300$ times more stable than $O_2$ -Hb complex.	
		Thus, it prevents hachloglobin to carry oxygen	
	Producer gas	from the lungs to other parts of the body.	

#### Uses:

- As a fuel in the form of water gas, producer gas etc.
- In the extraction of iron as reducing agent.

	8 8		
Carbon	$C + O_2 \xrightarrow{\Delta} CO_2$	$CO_2 + 2Mg \longrightarrow 2MgO + C$	- A+
dioxide	$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$	$CO_2 + H_2O \rightleftharpoons H_2CO_3$	: <u>Ö</u> C≡O: - (
(CO <sub>2</sub> )		$CO_2 + K_2CO_3 + H_2O \longrightarrow 2KHCO_3$	:Ö≝Ç≕Ö:
	$CaCO_3 + 2HCl \longrightarrow CaCl_2$	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$	<b>↑</b>
		$CO_2 + CaCO_3 + H_2O \longrightarrow Ca(HCO_3)_2$	:†o≡c− <u>ö:</u>
	06111706 / 207115011	$CO_2 + Zn \longrightarrow ZnO + CO$	(Linear structure with
	+ 2CO <sub>2</sub>	$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$	sp hybridisation)

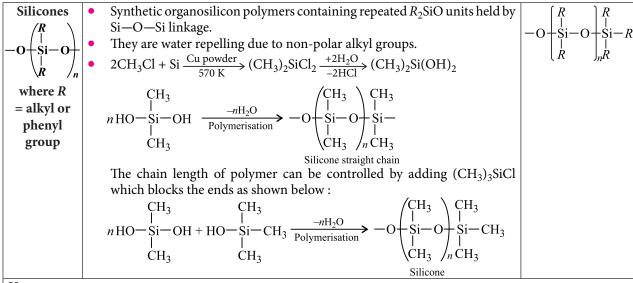
#### Uses:

- As carbogen [mixture of  $O_2$  ( $\approx$ 95%) +  $CO_2$  ( $\approx$ 5-10%)] in artificial respiration especially for pneumonia patients and victims of CO poisoning.
- As a fire extinguisher.

Silicon	It is a covalent, three dimensional network solid, almost non-reactive due to	-şi-O-şi-O-şi-
dioxide	high Si—O bond enthalpy. However, it is attacked by HF and NaOH.	
(SiO <sub>2</sub> , Silica)	$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$	-\si-O-\si-O-\si-
_	$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$	
		-\$i-O-\$i-O-\$i-

#### Uses:

- Quartz (crystallographic form of silica) is extensively used as a piezoelectric material.
- Silica gel is used as a drying agent and as a supporter for chromatographic materials and catalysts.
- Kieselguhr, an amorphous form of silica, is used in filtration plants.

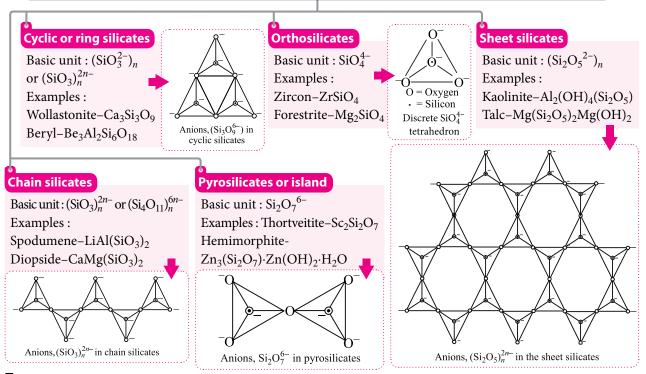


#### Uses:

• They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic implants.



Silicates are discrete  $SiO_4^{4-}$  tetrahedra or a number of such units joined together by sharing of oxygen.



#### ZEOLITES

- Zeolites are hydrated 3-dimensional aluminosilicates which are formed by replacing some of the silicon atoms by  $Al^{3+}$ ions. Their general formula is  $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot mH_2O$ .
- Zeolites are used as catalysts in petrochemical industries. They are also used as molecular sieves and softening of water by ion-exchange method.

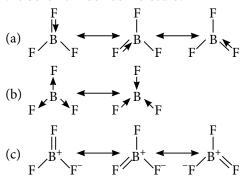


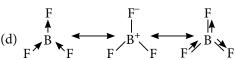
- 1. Which gas is evolved when PbO<sub>2</sub> is treated with conc. HNO<sub>3</sub>?
  - (a)  $NO_2$
- (b) O<sub>2</sub>
- (c)  $N_2$
- (d) N<sub>2</sub>O
- 2. In group-13, electronegativity first decreases from B to Al and then increases marginally down the group. This is because of
  - (a) non-metallic nature of B
  - (b) discrepancies in atomic size of elements
  - (c) ability of B and Al to form  $p\pi$   $p\pi$  multiple bonds
  - (d) irregular trend in electronegativity throughout the periodic table.
- 3. Which of the following statements is incorrect?
  - (a) The carbon dioxide molecule behaves as a non-polar molecule even though two of its resonating structures,  $\overset{+}{O} = C \overset{-}{O}$  and  $\overset{+}{O} = C \overset{-}{O}$ , are polar.
  - (b) Carbon dioxide is the anhydride of the unstable dibasic acid  $O = C(OH)_2$ .
  - (c) The carbon dioxide molecule is linear because the carbon atom utilises its *sp*-orbitals to form  $\sigma$ -bonds.
  - (d) The carbon atom is  $sp^2$ -hybridised in the  $CO_2$  molecule as well as in the molecule of its hydrate  $H_2CO_3$ .
- **4.** TlI<sub>3</sub>, a soluble ionic compound, in aqueous medium will give
  - (a) Tl<sup>3+</sup> and I<sup>-</sup> ions
- (b)  $Tl^+$ ,  $I^-$  and  $I_2$
- (c)  $Tl^{3+}$  and  $I_3$  ions
- (d)  $Tl^+$  and  $I_3^-$  ions.
- **5.** Among the following, the correct statement(s) is(are)
  - (a) Al(CH<sub>3</sub>)<sub>3</sub> has the three-centre two-electron bonds in its dimeric structure
  - (b) BH<sub>3</sub> has the three-centre two-electron bonds in its dimeric structure
  - (c) the Lewis acidity of BCl<sub>3</sub> is greater than that of AlCl<sub>3</sub>
  - (d) AlCl<sub>3</sub> has the three-centre two-electron bonds in its dimeric structure. (JEE Advanced 2017)
- **6.** Which of the following halides is least stable and has doubtful existence?
  - (a) CI<sub>4</sub>
- (b) GeI<sub>4</sub>
- (c) SnI<sub>4</sub>
- (d) PbI<sub>4</sub>

- 7. Incomplete combustion of petrol or diesel oil in automobile engines can be best detected by testing the fuel gases for the presence of
  - (a) carbon monoxide and water vapour
  - (b) carbon monoxide
  - (c) nitrogen dioxide
  - (d) sulphur dioxide.
- **8.** In  $BX_3$ , B X distance is shorter than what is expected theoretically because (X = F, Cl, Br, I)
  - (a) of  $sp^3$  hybridisation of B
  - (b) B *X* has a double bond character due to backbonding
  - (c) dimerisation takes place in  $BX_3$
  - (d) of large size of X, B X distance decreases.
- 9. An inorganic compound (*A*), composed of two most occurring elements in the earth's crust, have polymeric tetrahedral network structure. With carbon, compound (*A*) produces a poisonous gas (*B*) which is a stable diatomic molecule. Compounds (*A*) and (*B*) can be
  - (a)  $SiO_2$ ,  $CO_2$
- (b) SiO<sub>2</sub>, CO
- (c) SiC, CO
- (d)  $SiO_2$ ,  $N_2$
- **10.** The increasing order of atomic radii of the following group 13 elements is
  - (a) Al < Ga < In < Tl
  - (b) Ga < Al < In < Tl
  - (c) Al < In < Ga < Tl
  - (d) Al < Ga < Tl < In
- (JEE Advanced 2016)
- 11. In carbon-60, all carbon atoms are
  - (a)  $sp^2$ -hybridised with a truncated icosahedron shape
  - (b)  $sp^3$ -hybridised with a square antiprism shape
  - (c) sp<sup>2</sup>-hybridised with a diamond-like shape
  - (d)  $sp^2$ -hybridised with a graphite-like shape.
- **12.** AlF<sub>3</sub> is soluble in HF only in presence of KF. It is due to the formation of
  - (a)  $K_3[AlF_3H_3]$
- (b)  $K_3[AlF_6]$
- (c) AlH<sub>3</sub>
- (d) K[AlF<sub>3</sub>H]

(NEET Phase-II 2016)

- 13. An aqueous solution of borax is
  - (a) neutral
- (b) amphoteric
- (c) basic
- (d) acidic.
- **14.** Which of the following structures correctly represents the boron trifluoride molecule?





15. Consider the following standard electrode potentials ( $E^{\circ}$  in volts) in aqueous solution,

Element	$M^{3+}/M$	$M^+/M$
Al	-1.66	+0.55
Tl	+1.26	-0.34

Based on these data, which of the following statements is correct?

- (a) Tl<sup>+</sup> is more stable than Al<sup>+</sup>.
- (b) Tl<sup>3+</sup> is more stable than Al<sup>3+</sup>.
- (c) Al<sup>+</sup> is more stable than Al<sup>3+</sup>.
- (d) Tl<sup>+</sup> is more stable than Al<sup>3+</sup>.

#### (JEE Main online 2017)

- 16. Even though thermodynamically favourable, the conversion of diamond into graphite does not occur normally since
  - (a) the activation energy of the process is high.
  - (b) the activation energy of the process is low.
  - (c) the change of entropy is zero.
  - (d) the change of enthalpy is zero.
- 17. AlCl<sub>3</sub> achieves stability by forming a dimer. In trivalent state the compound is hydrolysed in water. The product formed is
  - (a) AlCl<sub>3</sub>·4H<sub>2</sub>O
- (b) AlCl<sub>3</sub>·6H<sub>2</sub>O
- (c) AlCl<sub>3</sub>·2H<sub>2</sub>O
- (d)  $Al_2O_3 + HCl$
- **18.** Select incorrect statement.
  - (a) Cyanamide ion,  $(CN_2)^{2-}$  is isoelectronic with CO<sub>2</sub> and has the same linear structure.
  - (b) Mg<sub>2</sub>C<sub>3</sub> reacts with water to form propyne.

- (c)  $CaC_2$  has  $C_2^{2-}$  and it contains one sigma and two pi bonds.
- (d) Al<sub>4</sub>C<sub>3</sub> is an example of methanide carbide and it contains  $C_4^{4-}$ .
- **19.** Which of the following statements is incorrect?
  - (a) B(OH)<sub>3</sub> partially reacts with water to form  $H_3O^+$  and  $[B(OH)_4]^-$ , and behaves like a weak
  - (b) B(OH)<sub>3</sub> behaves like a strong monobasic acid in the presence of sugars, and this acid can be titrated against NaOH solution using phenolphthalein as an indicator.
  - (c) B(OH)<sub>3</sub> does not donate a proton and hence does not form any salt with NaOH.
  - (d) B(OH)<sub>3</sub> reacts with NaOH, forming Na[B(OH)<sub>4</sub>].
- **20.** CCl<sub>4</sub> does not undergo hydrolysis but SiCl<sub>4</sub> is readily hydrolysed because
  - (a) carbon cannot expand its octet but silicon can expand
  - (b) electronegativity of carbon is higher than silicon
  - (c) *I.E.* of carbon is higher than that of silicon
  - (d) carbon forms double and triple bonds but not silicon.
- 21. Boric acid is an acid because its molecule
  - (a) contains replaceable H<sup>+</sup> ion
  - (b) gives up a proton
  - (c) accepts OH<sup>-</sup> from water releasing proton
  - (d) combines with proton from water molecule.

(NEET Phase-II 2016)

- **22.** Amongst the halides
  - (1) BCl<sub>3</sub> (2) AlCl<sub>3</sub> (3) GaCl<sub>3</sub> (4) InCl<sub>3</sub> the order of decreasing Lewis acid character is
  - (a) 1, 2, 3, 4
- (b) 4, 3, 2, 1
- (c) 3, 4, 2, 1
- (d) 2, 3, 4, 1
- 23.  $(COOH)_2 \xrightarrow{Conc. H_2SO_4} A + B + H_2O$ , concentration of A can be analysed by using iodine pentoxide, then incorrect statement about 'B' is
  - (a) solid B sublimes at 194.65 K
  - (b) *B* reacts with ammonia to form urea
  - supercritical *B* is used as solvent
  - (d) *B* is linear and neutral oxide.
- 24. What happens when a mixture of cobalt oxide and borax is heated in a flame on a loop of platinum wire?
  - (a) A transparent white bead is formed.
  - (b) A bright pink coloured NaBO<sub>2</sub> bead is formed.
  - (c) A blue coloured Co(BO<sub>2</sub>)<sub>2</sub> bead is formed.
  - (d) A red coloured Co(BO<sub>2</sub>)<sub>2</sub> bead is formed.

- **25.** The pair in which phosphorus atoms have a formal oxidation state of +3 is
  - (a) orthophosphorous and pyrophosphorous acids
  - (b) pyrophosphorous and hypophosphoric acids
  - (c) orthophosphorous and hypophosphoric acids
  - (d) pyrophosphorous and pyrophosphoric acids.

#### (JEE Main 2016)

- **26.** *X* reacts with aqueous NaOH solution to form *Y* and H<sub>2</sub>. Aqueous solution of *Y* on heating to 323-333 K and on passing CO<sub>2</sub> into it, Na<sub>2</sub>CO<sub>3</sub> and *Z* are formed. When *Z* is heated to 1200 °C, Al<sub>2</sub>O<sub>3</sub> is formed. *X*, *Y* and *Z* respectively are
  - (a) Al, AlCl<sub>3</sub>, NaAlO<sub>2</sub> (b) Zn, Na<sub>2</sub>ZnO<sub>2</sub>, Al(OH)<sub>3</sub>
  - (c) Al, Al(OH)<sub>3</sub>, AlCl<sub>3</sub> (d) Al, NaAlO<sub>2</sub>, Al(OH)<sub>3</sub>
- **27.** Ge(II) compounds are powerful reducing agents whereas Pb(IV) compounds are strong oxidants. This can be due to
  - (a) Pb is more electropositive than Ge
  - (b) ionisation potential of lead is less than that of Ge
  - (c) ionic radii of Pb<sup>2+</sup> and Pb<sup>4+</sup> are larger than those of Ge<sup>2+</sup> and Ge<sup>4+</sup>
  - (d) more pronounced inert pair effect in Pb than in Ge
- 28. CO<sub>2</sub> and N<sub>2</sub> are non-supporters of combustion. However, for putting out fires CO<sub>2</sub> is preferred over N<sub>2</sub> because CO<sub>2</sub>
  - (a) does not burn
  - (b) forms non-combustible products with burning substances
  - (c) is denser than nitrogen
  - (d) is a more reactive gas.
- 29. Alum helps in purifying water by
  - (a) forming Si complex with clay particles
  - (b) sulphate part which combines with dirt and removes it
  - (c) coagulating the mud particles
  - (d) making mud water soluble.
- 30. NaBH<sub>4</sub> + I<sub>2</sub>  $\xrightarrow{\text{in diglyme}} X + Y + Z$ BF<sub>3</sub> + NaH  $\xrightarrow{450 \text{ K}} X + P$ BF<sub>3</sub> + LiAlH<sub>4</sub>  $\rightarrow X + Q + R$

X, Y, Z, P, Q and R in the reactions are

Λ	Y	L	P	Q	K
(a) $Na_2B_4C$	7 NaI	HI	HF	LiF	$AlF_3$
(1.) D II	NT.T	TT	NT. F	T:F	4 1 T

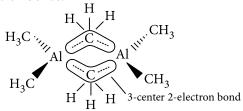
(b) B<sub>2</sub>H<sub>6</sub> NaI H<sub>2</sub> NaF LiF AlF<sub>3</sub>

(c) B<sub>2</sub>H<sub>6</sub> BH<sub>3</sub> NaI B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> Al<sub>2</sub>F<sub>6</sub> AlF<sub>3</sub>

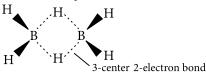
(d)  $BH_3$   $B_2H_6$   $H_2$   $B_3N_3H_6$  LiF All

#### **SOLUTIONS**

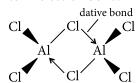
- 1. (b):  $2PbO_2 + 4HNO_3$  (conc.)  $\longrightarrow 2Pb(NO_3)_2 + 2H_2O + O_2$
- 2. (a): Name Formula Oxidation state
  Orthophosphorous acid  $H_3PO_3$  +3
  Pyrophosphoric acid  $H_4P_2O_5$  +3
  Hypophosphoric acid  $H_4P_2O_6$  +4
  Pyrophosphoric acid  $H_4P_2O_7$  +5
- 3. (d): Carbon atom is sp-hybridised in  $CO_2$  molecule and  $sp^2$ -hybridised in  $H_2CO_3$ .
- **4.** (d):  $TlI_3 \rightarrow Tl^+ + I_3^-$
- 5. (a, b, c): (a)  $Al_2(CH_3)_6$  has the three centre-two electron bonds.



(b) Dimer of BH<sub>3</sub> has 3-center 2-electron bond.



- (c) The size of element increases down the group, thus, Lewis acid character of BCl<sub>3</sub> is greater than that of AlCl<sub>3</sub>.
- (d) AlCl<sub>3</sub> has dative bond in its dimeric structure, not 3-center 2-electron bond.



- **6.** (d): It is because of inert pair effect.
- 7. **(b)**: Incomplete combustion of petrol or diesel gives carbon monoxide gas.
- **8. (b):** Due to back-bonding, B X bond in  $BX_3$  has a double bond character which, results in shorter B X distance.

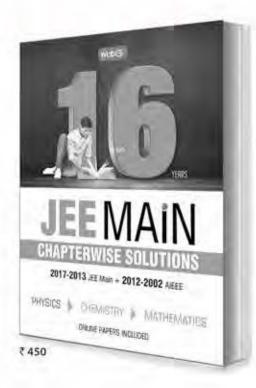
 $\stackrel{+}{X} = \overline{B} \stackrel{X}{\longleftrightarrow} X - \overline{B} \stackrel{X}{\longleftrightarrow} X - \overline{B} \stackrel{X}{\longleftrightarrow} X$ 

**9. (b):** The most abundant elements in the earth's crust are oxygen and silicon. They from SiO<sub>2</sub> which has polymeric tetrahedral network structure. This on heating with carbon forms SiC and CO.

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- 10. (b): The increasing order of atomic radii of group 13 elements is Ga < Al < In < Tl. Atomic radius of Ga is slightly lower than that of Al due to the presence of *d*-electrons in Ga which do not shield the nucleus effectively.
- 11. (a): In carbon-60, all carbon atoms  $sp^2$ -hybridised with a truncated icosahedron shape.
- 12. (b): AlF<sub>3</sub> is insoluble in anhydrous HF because the F ions are not available in hydrogen bonded HF but, in the presence of little amount of KF it forms soluble complex, K<sub>3</sub>[AlF<sub>6</sub>].  $AlF_3 + 3KF \rightarrow K_3[AlF_6]$
- 13. (c): An aqueous solution of borax is basic in nature due to the hydrolysis of  $B_4O_7^{2-}$  ions.
- 14. (a): BF<sub>3</sub> molecule involves extensive back bonding from fluorine to boron.
- 15. (a):  $Al^{3+}$  is more stable than  $Tl^{3+}$  because of negative  $E_{\rm Al^{3+}/Al}^{\circ}$  value.

Tl<sup>+</sup> is more stable than Al<sup>+</sup> because of negative  $E_{\text{Tl}^+/\text{Tl}}^{\circ}$  value.

- 17. (b): AlCl<sub>3</sub> in aqueous solution forms AlCl<sub>3</sub>·6H<sub>2</sub>O.  $Al_2Cl_6 + 12H_2O \rightarrow 2AlCl_3.6H_2O$
- 18. (d)
- 19. (c): Boric acid being acidic in nature forms salt (sodium metaborate) with NaOH.

$$B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$$
 or  $Na^+BO_2^- + 2H_2O$  Sodium metaborate

- 20. (a)
- 21. (c): Boric acid behaves as a Lewis acid, by accepting a pair of electrons from OH ion of water thereby releasing a proton.
- 22. (a): Lewis acid strength of group-13 halides follow the order:  $BCl_3 > AlCl_3 > GaCl_3 > InCl_3$ .
- 23. (d): CO<sub>2</sub> is an acidic oxide.

$$(COOH)_2 \xrightarrow{Conc. H_2SO_4} CO + CO_2 + H_2O$$
**24.** (c): Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O  $\xrightarrow{\Delta}$  Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>  $\xrightarrow{\Delta}$  2NaBO<sub>2</sub>

$$B_2O_3 + CoO \rightarrow Co(BO_2)_2$$
Cobalt metaborate
(blue bead)

**26.** (d): 
$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

$$2\text{NaAlO}_2 + \text{CO}_2 + 3\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{Al(OH)}_3 + \text{Na}_2\text{CO}_3$$

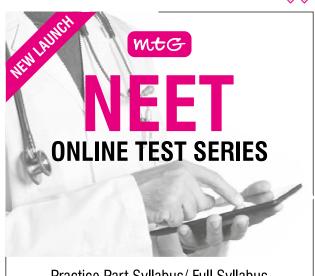
$$(Y) \qquad (Z)$$

$$2\text{Al(OH)}_3 \xrightarrow{1200^{\circ}\text{C}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$

- 27. (d): Ge<sup>4+</sup> is more stable than Ge<sup>2+</sup> as a result of which Ge<sup>2+</sup> has a tendency to be oxidised to Ge<sup>4+</sup>, so Ge2+ compounds act as powerful reducing agents. But Pb2+ is more stable than Pb4+ because of pronounced inert pair effect as a result of which Pb<sup>4+</sup> has a tendency to get reduced to Pb<sup>2+</sup> so Pb<sup>4+</sup> compounds act as strong oxidising agents.
- **28.** (c):  $CO_2$  is denser than  $N_2$  and air thus surrounds the igniting material more effectively.
- 29. (c): Alums help in purifying water by coagulating the negatively charged mud particles by Al<sup>3+</sup> ions provided by it.

30. (b): 
$$2\text{NaBH}_4 + I_2 \xrightarrow{\text{in diglyme} \text{solution}} B_2H_6 + 2\text{NaI} + H_2 \xrightarrow{(X)} 2BF_3 + 6\text{NaH} \xrightarrow{450 \text{ K}} B_2H_6 + 6\text{NaF} \xrightarrow{(Z)} (P)$$

$$4BF_3 + 3\text{LiAlH}_4 \rightarrow 2B_2H_6 + 3\text{LiF} + 3\text{AlF}_3$$



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# **EXAMINER'S**

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.			
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.			
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.			
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.			
Section - V	<ul> <li>Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as:</li> <li>(a) If both assertion and reason are true and reason is the correct explanation of assertion.</li> <li>(b) If both assertion and reason are true but reason is not the correct explanation of assertion.</li> <li>(c) If assertion is true but reason is false.</li> <li>(d) If both assertion and reason are false.</li> </ul>			
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).			

#### **EQUILIBRIUM**

#### **SECTION - I**

#### **Only One Option Correct Type**

- 1. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?
  - (a)  $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
  - (b)  $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
  - (c)  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
  - (d) All of these
- 2. a moles of PCl<sub>5</sub> are heated in a closed container to equilibrate  $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$  at a pressure of P atm. If x moles of PCl<sub>5</sub> dissociate at equilibrium,

(a) 
$$\frac{x}{a} = \frac{K_p}{K_p + P}$$

(a) 
$$\frac{x}{a} = \frac{K_p}{K_p + P}$$
 (b)  $\frac{x}{a} = \left(\frac{K_p + P}{K_p}\right)^{1/2}$ 

(c) 
$$\frac{x}{a} = \left(\frac{K_p}{P}\right)^{1/2}$$

(c) 
$$\frac{x}{a} = \left(\frac{K_p}{P}\right)^{1/2}$$
 (d)  $\frac{x}{a} = \left(\frac{K_p}{K_p + P}\right)^{1/2}$ 

3. At 350 K,  $K_p$  for the reaction given below is  $3.0 \times 10^{10} \text{ bar}^{-1}$  at equilibrium. What will be the value of  $K_c$  at this temperature?

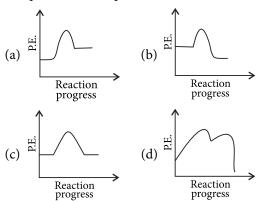
$$2N_{2(g)} + O_{2(g)} \rightleftharpoons 2N_2O_{(g)}$$

- (a)  $7.4 \times 10^{11} \,\mathrm{L \ mol^{-1}}$
- (b)  $8.715 \times 10^{10} \,\mathrm{L \, mol^{-1}}$
- (c)  $0.08 \,\mathrm{L \, mol^{-1}}$
- (d)  $8.715 \times 10^{11} \,\mathrm{L \, mol^{-1}}$
- What is the correct sequence, to complete the paragraph? According to Le-Chatelier's principle, if pressure is increased,
  - (1) if pressure is decreased, the system will try to increase the pressure
  - (2) the system will try to reduce the pressure
  - (3) by favouring that reaction which is accompanied by a decrease in the number of moles
  - (4) by favouring that reaction which is accompanied by an increase in the number of moles.
  - (a) 2314
- (b) 1234
- (c) 1432
- (d) 1324
- 5. Dissociation constant values of few acids are given below. Arrange them in order of increasing acidic strength.

 $(K_a \text{ values} : H_2SO_3 = 1.3 \times 10^{-2}, \text{HNO}_2 = 4 \times 10^{-4},$  $CH_3COOH = 1.8 \times 10^{-5}, HCN = 4 \times 10^{-10})$ 

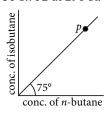
- (a)  $HCN < CH_3COOH < HNO_2 < H_2SO_3$
- (b)  $CH_3COOH < HNO_2 < HCN < H_2SO_3$
- (c) CH<sub>3</sub>COOH < HCN < H<sub>2</sub>SO<sub>3</sub> < HNO<sub>2</sub>
- (d)  $HNO_2 < H_2SO_3 < CH_3COOH < HCN$

- 6. Solid Ba(NO<sub>3</sub>)<sub>2</sub> is gradually dissolved in  $1.0 \times 10^{-4}$  M Na<sub>2</sub>CO<sub>3</sub> solution. At what concentration of Ba<sup>2+</sup> the precipitate will begin to form?  $(K_{sp} \text{ for BaCO}_3 = 5.1 \times 10^{-9})$ 
  - (a)  $^{1}4.1 \times 10^{-5} \text{ M}$
- (b)  $5.1 \times 10^{-5} \text{ M}$
- (c)  $8.1 \times 10^{-8} \text{ M}$
- (d)  $8.1 \times 10^{-7} \text{ M}$
- 7. Which of the following reflects that the reaction is independent of temperature?



For the equilibrium,  $CH_3 - CH_2 - CH_2 - CH_{3(g)} \rightleftharpoons CH_3$ 

equilibrium constant is found to be 1.732 at 298 K. Now if in a vessel at 298 K, a mixture of these two gases is taken and the point p is represented in the given figure, predict what will happen?



- (a) Immediately equilibrium will set-up.
- (b) The given reaction will go in the forward direction till it attains equilibrium.
- (c) The given reaction will go in the backward direction till it attains equilibrium.
- (d) Cannot be predicted.
- 9. Calculate the degree of dissociation of PCl<sub>5</sub>, when the density at 230 °C is 70.
  - (a) 97.8%
- (b) 48.9%
- (c) 4.89%
- (d) 24.45%
- 10. The correct order of increasing  $[H_3O^+]$  in the following aqueous solutions is
  - (a)  $0.01 \text{ M H}_2\text{S} < 0.01 \text{ M H}_2\text{SO}_4 < 0.01 \text{ M NaCl}$ < 0.01 M NaNO<sub>2</sub>
  - (b) 0.01 M NaCl < 0.01 M NaNO<sub>2</sub> < 0.01 M H<sub>2</sub>S < 0.01 M H<sub>2</sub>SO<sub>4</sub>

- (c) 0.01 M NaNO<sub>2</sub> < 0.01 M NaCl < 0.01 M H<sub>2</sub>S < 0.01 M H<sub>2</sub>SO<sub>4</sub>
- (d) 0.01 M H<sub>2</sub>S < 0.01 M NaNO<sub>2</sub> < 0.01 M NaCl < 0.01 M H<sub>2</sub>SO<sub>4</sub>

#### **SECTION - II**

#### More than One Options Correct Type

- 11. For the reaction,  $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ , the value of K is 50 at 400 K and 1700 at 500 K. Which of the following options are correct?
  - (a) The reaction is endothermic.
  - (b) The reaction is exothermic.
  - (c) If  $NO_{2(g)}$  and  $N_2O_{4(g)}$  are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more  $N_2O_{4(g)}$  will be formed.
  - (d) The entropy of the system remains constant.
- 12. The thermal decomposition of  $CaCO_{3(s)}$  is studied under different conditions,

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

For this equilibrium, the correct statements are

- (a)  $\Delta H$  is dependent on T
- (b) K is independent of the initial amount of CaCO<sub>3</sub>
- (c) K is dependent on the pressure of CO<sub>2</sub> at a
- (d)  $\Delta H$  is independent of the catalyst, if any.
- 13. The equilibrium constants of the reactions,

$$N_2 + 3H_2 \Longrightarrow 2NH_3$$
 and  $\frac{1}{2}N_2 + \frac{3}{2}H_2 \Longrightarrow NH_3$ 

are  $K_1$  and  $K_2$  respectively. The relationship between  $K_1$  and  $K_2$  is

- (a)  $K_1 = K_2$
- (b)  $K_2 = \sqrt{K_1}$
- (c)  $K_1 = K_2^2$
- (d)  $K_1 = \sqrt{K_2}$

#### **SECTION - III**

#### Paragraph Type

#### Paragraph for Questions 14 and 15

A number of acid-base concepts have been put forward from time to time. Arrhenius laid emphasis on H<sup>+</sup> ions and OH<sup>-</sup> ions, whereas Bronsted and Lowry considered acids and bases as proton donors and acceptors and also suggested the concept of conjugate acid-base pairs. Lewis concept was the electronic concept. The first two concepts could also explain the strengths of acids and bases. Arrhenius could explain in terms of dissociation constants of the acids and bases whereas Bronsted-Lowry could do it by suggesting that a strong acid has a weak conjugate base and vice-versa.

- **14.** In the reaction  $I_2 + I^- \longrightarrow I_3^-$ , the Lewis base is (b)  $I^{-}$  (c)  $I_{3}^{-}$ (a) I<sub>2</sub> (d) none.
- **15.** The successive dissociation constants  $K_{a_1}$ ,  $K_{a_2}$  and  $K_{a_3}$  of orthophosphorous acid (H<sub>3</sub>PO<sub>3</sub>) could be
  - (a)  $7 \times 10^{-7}$ ,  $1.6 \times 10^{-2}$ , 0
  - (b)  $1.6 \times 10^{-2}$ ,  $7 \times 10^{-7}$ , 0
  - (c)  $1.6 \times 10^{-2}$ ,  $7 \times 10^{-7}$ ,  $1 \times 10^{-12}$
  - (d)  $1 \times 10^{-12}$ ,  $7 \times 10^{-7}$ ,  $1.6 \times 10^{-2}$

#### Paragraph for Questions 16 and 17

Two solids *X* and *Y* dissociate into gaseous products at a certain temperature as follows:

- (i)  $X_{(s)} \rightleftharpoons A_{(g)} + C_{(g)}$  and
- (ii)  $Y_{(s)} \rightleftharpoons B_{(g)} + C_{(g)}$

At a given temperature, total pressure over solid 'X' is 40 mm of Hg and total pressure over solid 'Y' is 60 mm of Hg. Now, answer the following questions:

- **16.** Ratio of  $K_p$  for reaction (i) to that of reaction (ii), is (b) 2:3 (c) 3:2
- 17. The ratio of moles of A and B in the vapour state over a mixture of solids *X* and *Y*, is
  - (a) 2:3
- (b) 2:5
- (c) 4:9
  - (d) 1:1

#### **SECTION - IV Matching List Type**

18. Match the List I with List II and select the correct answer using the codes given below the lists:

#### List I

- (P)  $2NO \rightleftharpoons N_2 + O_2$
- $K_p = K_c/RT$
- (Q)  $N_2 + 3H_2 \rightleftharpoons 2NH_3$
- (ii)  $K_p = K_c RT$
- (R)  $PCl_3 + Cl_2 \rightleftharpoons PCl_5$
- (iii)  $K_p = K_c$
- (S)  $2O_3 \rightleftharpoons 3O_2$
- (iv)  $K_D = K_C (RT)^{-2}$

- P Q R

(a) (iii)

(i) (ii)

S

- (iv) (b) (i) (ii) (iii) (iv)
- (c) (iv) (iii) (i) (ii)
- (d) (ii) (i) (iv) (iii)
- **MPP-8 CLASS XII ANSWER KEY** (b) **5.** (b) 1. (a) (d) (d) **6.** (b) 7. (a) (c) (b) **10.** (a) 8. **11.** (c) **12.** (a) **13.** (c) 14. (d) **15.** (b) **16.** (a) **17.** (b) **18.** (d) **19.** (b) **20.** (b,d) **21.** (a,b) **22.** (a,c) 23. (c,d)(1) **25.** (3) **26.** (1) **27.** (d) **28.** (b) **29.** (d) **30.** (c)

19. Match the List I with List II and select the correct answer using the codes given below the lists:

#### List I

List II

- (P) Solubility of Hg<sub>2</sub>Cl<sub>2</sub> in  $10~K_{sp}$ 0.1 M NaCl solution.
- Solubility of PbI<sub>2</sub> in 0.01 M  $100~K_{sp}$ KI solution.
- Solubility of Ag<sub>2</sub>CrO<sub>4</sub> in (R) (iii)  $10000 K_{sp}$ 0.25 M K<sub>2</sub>CrO<sub>4</sub> solution.
- Solubility of calcium (S) oxalate in 0.1 M oxalic acid solution.
  - S P Q R
- (a) (ii) (i) (iii) (iv)
- (b) (iii) (ii) (i) (iv)
- (c) (ii) (iv) (iii) (i)
- (d) (i) (iii) (iv) (ii)

#### **SECTION - V**

#### **Assertion Reason Type**

**20. Assertion**: The second dissociation constant of fumaric acid is greater than maleic acid.

**Reason:** Higher the dissociation constant of acid more is acidic character.

- **21. Assertion**: The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid. Reason: Hydrogen sulphide is a weak acid.
- 22. Assertion: The pH of an aqueous solution of acetic acid remains unchanged on addition of sodium acetate. Reason: The ionisation of acetic acid is increased by addition of sodium acetate.

#### **SECTION - VI**

#### **Integer Value Correct Type**

- **23.** In 1 L saturated solution of AgCl  $[K_{sp}(AgCl)]$ = 1.6 × 10<sup>-10</sup>], 0.1 mol of CuCl  $[K_{sp}^{(r)}(CuCl)]$  $=1.0 \times 10^{-6}$ ] is added. The resultant concentration of Ag<sup>+</sup> in the solution is  $1.6 \times 10^{-x}$ . The value of x is
- 24. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is

KCN K<sub>2</sub>SO<sub>4</sub>  $(NH_4)_2C_2O_4$ NaCl  $Zn(NO_3)_2$ FeCl<sub>3</sub> K<sub>2</sub>CO<sub>3</sub> NH<sub>4</sub>NO<sub>3</sub> LiCN

25. Find the total number of diprotic acids among the following:

H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub>, H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, H<sub>3</sub>BO<sub>3</sub>, H<sub>3</sub>PO<sub>2</sub>, H<sub>2</sub>CrO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>

#### THE p-BLOCK ELEMENTS

#### **SECTION - I**

#### **Only One Option Correct Type**

- 1. Which of the following elements is not likely to act as central atom in  $MF_6^{3-}$ ?
  - (a) B
- (b) Al
- (c) Ga
- (d) In
- 2. An aqueous solution of boric acid is found to be weakly acidic in nature. This acidic character arises due to which of the following reasons?
  - (a) It is a protic acid which donates protons in aqueous solution.
  - (b) It is a Lewis acid which accepts OH<sup>-</sup> from water and leaves H<sup>+</sup> to make the solution acidic.
  - (c) It gives metaboric acid when dissolved in water.
  - (d) It is prepared by reaction of borax with sulphuric acid hence, it behaves as an acid.
- 3. Which of the following statements is false?
  - (a) Silicon carbide has a three dimensional structure with each silicon and carbon atoms being tetrahedrally surrounded by four atoms of the other kind.
  - (b) Carbon can form C = S bond because C has the ability to form  $d\pi d\pi$  bonds.
  - (c) Boron nitride has a structure similar to graphite.
  - (d) Graphite conducts electricity because of the availability of delocalised  $\pi$ -electrons.
- **4.** A solid element Y conducts electricity and forms two chlorides,  $YCl_n$  (a colourless volatile liquid) and  $YCl_{n-2}$  (a colourless solid). Then the element Y is
  - (a) C
- (b) Sn
- (c) B
- (d) Al
- **5.** Aluminium oxide is not reduced by chemical reactions since
  - (a) reducing agent contaminate
    - (b) the process pollute the environment
    - (c) aluminium oxide is highly stable
    - (d) aluminium oxide is reactive.
- 6. An alkali metal hydride (NaH) reacts with diborane in 'A' to give a tetrahedral compound 'B' which is extensively used as reducing agent in organic synthesis. The compound 'A' and 'B' respectively are

- (a) CH<sub>3</sub>COCH<sub>3</sub> and B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>
- (b)  $(C_2H_5)_2O$  and NaBH<sub>4</sub>
- (c) C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>Na
- (d) C<sub>6</sub>H<sub>6</sub> and NaBH<sub>4</sub>
- 7. Predict *X* and *Y* in the following reaction?  $3B_2H_6 + 6X \xrightarrow{\text{Low temp.}} 3[BH_2(X)_2]^+[BH_4]^{-\frac{473 \text{ K}}{2}} Y + 12H_2$ 
  - (a)  $X = NH_3$ ,  $Y = B_3N_3H_6$
  - (b) X = CO,  $Y = BH_3 \cdot CO$
  - (c) X = NaH, Y = NaF
  - (d)  $X = NF_3$ ,  $Y = B_3N_3$
- 8. Which of the following statements is incorrect?
  - (a) Silicones are polymeric organosilicon compounds.
  - (b) SiF<sub>4</sub> has tetrahedral shape.
  - (c)  $Pb^{2+}$  is less stable than  $Sn^{2+}$ .
  - (d) Mg<sub>2</sub>C<sub>3</sub> is an allylide type of ionic carbide.
- 9. The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol<sup>-1</sup>) of C-C, Si-Si and Ge-Ge are respectively
  - (a) 260, 297, 348
- (b) 297, 260, 348
- (c) 348, 260, 297
- (d) 348, 297, 260
- 10. Unlike the other elements of its group, carbon does not form  $CX_2$  type molecules because
  - (a) energetically this is not possible
  - (b) carbon undergoes catenation
  - (c) it is non-metallic
  - (d) carbon does not contain *d*-orbital.

#### SECTION - II

#### More than One Options Correct Type

- **11.** Me<sub>3</sub>SiCl is used during polymerisation of organosilicones because
  - (a) the chain length of organosilicone polymers can be controlled by adding Me<sub>3</sub>SiCl
  - (b) Me<sub>3</sub>SiCl blocks the end terminal of silicone polymer
  - (c) Me<sub>3</sub>SiCl improves the quality and yield of the polymer
  - (d) Me<sub>3</sub>SiClacts as a catalyst during polymerisation.
- 12. Which of the following statements are correct?
  - (a)  $PbO_2$  is a strong oxidising agent.
  - (b) CO<sub>2</sub> is non-poisonous and neutral in character.
  - (c) GeCl<sub>2</sub> is a strong reductant.
  - (d) B(OH)<sub>3</sub> gives weak alkaline solution.

- 13. Which of the following statements are correct?
  - (a) Group-13 elements show only one oxidation state *i.e.*, +3.
  - (b) Tl(III) salts undergo disproportionation.
  - (c) SiO<sub>2</sub> is covalent solid.
  - (d) B(OMe)<sub>3</sub> imparts green colour to Bunsen flame.

#### **SECTION - III**

#### Paragraph Type

#### Paragraph for Questions 14 and 15

The maximum or the highest oxidation state shown by an element of *p*-block is equal to the total number of valence electrons. In Groups-13 and 14, the group oxidation state is the most stable for the lighter elements of the group but as we move down in a group, a lower oxidation state, which is two unit less than the group oxidation state, becomes progressively more stable for heavier elements. This is due to inert pair effect.

- **14.** Which among the following is the strongest oxidising agent?
  - (a) SnO<sub>2</sub>
- (b) SiO<sub>2</sub>
- (c) GeO<sub>2</sub>
- (d) PbO<sub>2</sub>
- 15. Which of the following is the most acidic oxide?
  - (a) CO<sub>2</sub>
- (b) SiO<sub>2</sub>
- (c) PbO<sub>2</sub>
- (d)  $SnO_2$

#### Paragraph for Questions 16 and 17

Boron halides are electron-deficient compounds and act as Lewis acids. In boron halides, there is double bond character between boron and halogen atom because of the back bonding. Even the weakest bases will form adducts with the trihalides of boron. The rehybridisation of boron that accompanies adduct formation results in a loss of B—X double bond character.

**16.** In the adduct formation of trimethyl amine with boron halide,

 $BX_3 + : N(CH_3)_3 \longrightarrow X_3B : N(CH_3)_3$ 

the enthalpy change is more negative in the case of

- (a) BF<sub>3</sub>
- (b) BCl<sub>3</sub>
- (c) BBr<sub>3</sub>
- (d) all are equal.
- 17. BF<sub>3</sub> exists as monomer but not as dimer because
  - (a) of back bonding
  - (b) BF<sub>3</sub> is ionic compound
  - (c) of steric hindrance
  - (d) none of these.

#### **SECTION - IV**

#### Matching List Type

**18.** Match the List I with List II and select the correct answer using the codes given below the lists:

(i)

#### List I

#### List II

- (P) Diborane
- Used as a flux for soldering metals
- (Q) Gallium
- (ii) Banana bonds
- (R) Borax

P

- (iii) Low melting and high boiling point, useful for measuring high temperatures
- Aluminosilicate (iv) Used as a catalyst in petrochemical industries

#### Q R S

- (a) (ii) (i) (iii) (iv)
- (b) (ii) (iii) (i) (iv)
- (c) (i) (iii) (iv) (ii)
- (d) (iv) (ii) (i) (iii)
- **19.** Match the List I with List II and select the correct answer using the codes given below the lists:

#### List I

#### List II

- (P) Aluminosilicate (i) glass
- Cheap laboratory apparatus
- (Q) Calcium alkali (ii) silicate
- Optical glasses
- (R) Lead glass
- (iii) Domestic glass for windows
- (S) Soda glass
- (iv) Low coefficient of expansion

#### P Q R S

- (a) (iv) (iii) (ii) (i)
- (b) (i) (iv) (iii) (ii)
- (c) (ii) (i) (iv) (iii)
- (d) (iii) (ii) (iv)

#### **SECTION - V**

#### **Assertion Reason Type**

20. Assertion: If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

**Reason :** Aluminium is trivalent while silicon is tetravalent.

**21. Assertion**: Although aluminium is above hydrogen in electrochemical series, it is stable in air and water.

**Reason :** The thin protective layer of its oxide  $(Al_2O_3)$  on the surface, protects the aluminium.

**22. Assertion**: In  $CO_2$  molecule, C-atom undergoes  $sp^2$  hybridisation.

**Reason**: CO<sub>2</sub> molecule has net dipole moment.

#### **SECTION - VI**

#### **Integer Value Correct Type**

- **23.** The total number of protons donated by one molecule of boric acid (H<sub>3</sub>BO<sub>3</sub>) is
- **24.** The compound  $(CH_3)_nSi(Cl)_{4-n}$  on hydrolysis gives a branched chain silicone. The value of n is
- **25.** The oxidation state of C in CO is x. The oxidation state of C in  $COCl_2$  is y. Then, the value of y x is

#### **SOLUTIONS**

#### **EQUILIBRIUM**

- 1. (d): The equilibrium will remain unaffected in all three reactions on addition of small amount of argon (inert gas) at constant volume.
- 2. (d):  $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$   $1-\alpha$   $\alpha$   $\alpha$ ( $\alpha$  = degree of dissociation)

Total moles =  $1 - \alpha + \alpha + \alpha = 1 + \alpha$ 

$$K_{p} = \frac{p_{\text{PCl}_{3}} \times p_{\text{Cl}_{2}}}{p_{\text{PCl}_{5}}} = \frac{\left[\frac{\alpha}{1+\alpha}P\right] \left[\frac{\alpha}{1+\alpha}P\right]}{\frac{1-\alpha}{1+\alpha}P}$$

$$= \frac{\alpha^2 P}{1 - \alpha^2} \Rightarrow \alpha = \left(\frac{K_p}{K_p + P}\right)^{1/2} \qquad \dots (i)$$

Given, a moles of PCl<sub>5</sub> are heated then x moles of it dissociate at equilibrium.

Hence, 
$$\alpha = \frac{x}{a}$$

Thus, equation (i) becomes,

$$\frac{x}{a} = \left(\frac{K_p}{K_p + P}\right)^{1/2}$$

3. (d):  $K_p = K_c (RT)^{\Delta n}$ ;  $\Delta n = 2 - 3 = -1$  $T = 350 \text{ K}, R = 0.083 \text{ L bar K}^{-1} \text{mol}^{-1}$ 

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$K_c = \frac{3 \times 10^{10} \text{ bar}^{-1}}{(0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 350 \text{ K})^{-1}}$$

$$= 3 \times 10^{10} \text{ bar}^{-1} \times 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 350 \text{ K}$$

$$= 8.715 \times 10^{11} \text{ L mol}^{-1}$$

- 4. (a)
- **5.** (a): Acidic strength  $\propto K_a$

- 6. **(b)**:  $K_{sp}$  for BaCO<sub>3</sub> = [Ba<sup>2+</sup>][CO<sub>3</sub><sup>2-</sup>] Given, [CO<sub>3</sub><sup>2-</sup>] = 1 × 10<sup>-4</sup> M (from Na<sub>2</sub>CO<sub>3</sub>)  $K_{sp} = 5.1 \times 10^{-9}$   $\therefore 5.1 \times 10^{-9} = [Ba^{2+}] \times 10^{-4}$   $\Rightarrow [Ba^{2+}] = 5.1 \times 10^{-5} M$ Thus, at [Ba<sup>2+</sup>] = 5.1 × 10<sup>-5</sup> M, BaCO<sub>3</sub> will starts precipitating.
- 7. (c):  $\Delta H = 0$ , it means reaction is independent of temperature.
- **8.** (c): From given information,

$$\tan 75^\circ = 3.73 = \frac{\text{conc. of isobutane}}{\text{conc. of } n\text{-butane}} > K_c$$

So, reaction will proceed in backward direction.

9. **(b)**: Degree of dissociation ( $\alpha$ ) =  $\frac{D-d}{(n-1)d}$ 

where n = no. of moles of gaseous products produced by 1 mole of reactant.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
1 mol 1 mol 1 mol
i.e.,  $n = 2$ 

$$D(\text{vapour density}) = \frac{\text{Mol. wt.}}{2} = \frac{208.5}{2} = 104.25$$

$$\alpha = \frac{104.25 - 70}{(2 - 1)70} = 0.489$$

Percentage dissociation =  $0.489 \times 100 = 48.9\%$ 

- 10. (c): H<sub>2</sub>SO<sub>4</sub> is a strong acid having pH < 7. NaNO<sub>2</sub> on hydrolysis gives alkaline solution of pH > 7. NaCl is a neutral salt so, pH = 7 and H<sub>2</sub>S is a weak acid so, pH will be slightly lesser than 7.
- **11. (a, c): (a)** For an endothermic reaction, *K* increases with increase in temperature.

(c) At 400 K, 
$$Q = \frac{(p_{\text{NO}_2})^2}{(p_{\text{NO}_2})} = \frac{(20)^2}{2} = 200$$

As Q > K, hence, reaction proceeds in backward direction.

- 12. (a, b, d):  $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ The equilibrium constant (K) is independent of the initial amount of CaCO3 whereas at a given temperature, it is independent of pressure of CO<sub>2</sub>.  $\Delta H$  is independent of catalyst and it depends on temperature.
- **13.** (**b**, **c**) :  $N_2 + 3H_2 \rightleftharpoons 2NH_3$  $\therefore K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$  $\frac{1}{2}N_2 + \frac{3}{2}H_2 \Longrightarrow NH_3$  $\therefore K_2 = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \sqrt{K_1} \implies K_1 = K_2^2$
- 14. (b): I donates an electron pair hence, it acts as a
- **15.** (b):  $K_{a_1} > K_{a_2}$  and  $K_{a_3} = 0$  (because H<sub>3</sub>PO<sub>3</sub> is a dibasic acid).
- **16.** (a):  $X_{(s)} \rightleftharpoons A_{(g)} + C_{(g)}$ 20 mm 20 mm  $K_{p_1} = 20 \times 20 = 400 \text{ mm}^2 \text{ and}$  $Y_{(s)} \rightleftharpoons B_{(g)} + C_{(g)}$ 30 mm 30 mm  $K_{p_2} = 30 \times 30 = 900 \text{ mm}^2$  $\therefore \frac{K_{p_1}}{K_p} = \frac{4}{9}$
- 17. (c): In mixture, solids X and Y dissociate simultaneously,

On dividing eqn. (i) by (ii), we get

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{p_1}{p_2} = \frac{4}{9} = \frac{y_A}{y_B}$$

18. (a)

19. (a): (P) 
$$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^ K_{sp} = [Hg_2^{2+}] [Cl^-]^2 = s(0.1 + 2s)^2 \approx (0.1)^2 s$$
 $\therefore s = 100 K_{sp}$ 
(Q)  $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$ 

$$K_{sp} = [Pb^{2+}] [I^{-}]^{2} = s(0.01 + 2s)^{2} \approx s(0.01)^{2}$$

$$= 10^{-4} s$$

$$\therefore s = 10^{4} K_{sp}$$
(R)  $Ag_{2}CrO_{4} \rightleftharpoons 2Ag^{+} + CrO_{4}^{2-}$ 

$$K_{sp} = [Ag^{+}]^{2} [CrO_{4}^{2-}]$$

$$= (2s)^{2} (0.25 + s) \approx (2s)^{2} (0.25)$$
or  $s = \sqrt{K_{sp}}$ 
(S)  $CaC_{2}O_{4} \rightleftharpoons Ca^{2+} + C_{2}O_{4}^{2-}$ 

$$K_{sp} = [Ca^{2+}] [C_{2}O_{4}^{2-}]$$

$$= s(0.1 + s) \approx 0.1s \text{ or } s = 10 K_{sp}$$

- 20. (a): Both fumaric and maleic acids have two ionisable H<sup>+</sup> ions *i.e.*, protons. The maleate monoanion shows intramolecular H-bonding, whereas fumarate monoanion shows intermolecular H-bonding. Thus, fumarate monoanion requires more energy to give fumarate dianion. Hence, second dissociation of fumaric acid is more than that of maleic acid.
- 21. (b)
- 22. (d): Addition of a small amount of CH<sub>3</sub>COONa to acetic acid increases the pH value because CH<sub>3</sub>COONa is a strong electrolyte and thus, ionises to give CH<sub>3</sub>COO<sup>-</sup> and Na<sup>+</sup> ions. Due to common ion effect, it suppresses the ionisation of CH<sub>3</sub>COOH which decreases [H<sup>+</sup>] and hence, pH value increases.
- 23. (7): Let the solubility of AgCl and CuCl be  $a \text{ mol litre}^{-1}$  and  $b \text{ mol litre}^{-1}$  respectively.

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-}; CuCl \rightleftharpoons Cu^{+} + Cl^{-}$$

$$a \quad a$$

$$\therefore \quad K_{sp} \text{ of } AgCl = [Ag^{+}] [Cl^{-}]$$

$$1.6 \times 10^{-10} = a(a+b) \qquad ...(i)$$
Similarly,  $K_{sp}$  of CuCl =  $[Cu^{+}][Cl^{-}]$ 

$$1.0 \times 10^{-6} = b(a+b) \qquad ...(ii)$$

$$\frac{a}{b} = 1.6 \times 10^{-4}$$
 or  $a = 1.6 \times 10^{-4} \times b$ 

Substituting the value of *a* in eqn. (i), we get  $1.6 \times 10^{-10} = 1.6 \times 10^{-4} \ b (1.6 \times 10^{-4} \ b + b)$  $\Rightarrow 10^{-6} = b^2 (1.6 \times 10^{-4} + 1)$  $\Rightarrow b = 10^{-3} [:: 1.6 \times 10^{-4} <<< 1] \Rightarrow a = 1.6 \times 10^{-7}$  $[Ag^{+}] = a = 1.6 \times 10^{-7}$ ; Comparing with  $1.6 \times 10^{-x}$  $\Rightarrow x = 7$ 

**24.** (3): Salts of strong base and weak acid give basic solution.

$$KCN + H_2O \longrightarrow KOH + HCN$$
  
 $K_2CO_3 + 2H_2O \longrightarrow 2KOH + H_2CO_3$   
 $LiCN + H_2O \longrightarrow LiOH + HCN$ 

**25.** (6): Diprotic acids are those which furnish two protons per molecule like, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub>, H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>CrO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>.

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$
 (monobasic)

$$\begin{array}{c} O \\ || \\ || \\ OH \\ OH \\ \\ H_3PO_2: H-P-OH \ (monobasic) \\ || \\ H \end{array}$$

#### THE p-BLOCK ELEMENTS

- 1. (a): Boron cannot expand its coordination number beyond 4 due to absence of d-orbitals. Therefore, it can not act as central metal atom in  $MF_6^{3-}$ .
- 2. (b): It reacts with water to accept OH<sup>-</sup> ions and releases H<sub>3</sub>O<sup>+</sup> ions to make acidic solution.

$$B(OH)_3 + 2H_2O \longrightarrow H_3O^+ + [B(OH)_4]^-; pK_a = 9.25$$

- 3. (b): Carbon does not have *d*-orbitals to form  $d\pi d\pi$  bonds.
- **4. (b):** Element *Y* is tin which conducts electricity and can exist in +2 and +4 oxidation state. SnCl<sub>4</sub> is colourless volatile liquid whereas SnCl<sub>2</sub> is colourless ionic solid.
- 5. (c)
- 6. **(b)**:  $2\text{NaH} + \text{B}_2\text{H}_6 \xrightarrow{(\text{C}_2\text{H}_5)_2\text{O}(A)} 2\text{NaBH}_4$ Sodium borohydride

  (B)
- 7. (a):  $3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^ \downarrow^{\text{Heat}}$   $2B_3N_3H_6 + 12H_2$  (Y)
- **8.** (c): Stability of +2 oxidation state increases down the group-14 due to inert pair effect thus, Pb<sup>2+</sup> is more stable than Sn<sup>2+</sup>.
- **9.** (d): Catenation tendency decreases with the decrease in *M*–*M* bond energy. Hence, bond

- energies of C-C, Si-Si and Ge-Ge are 348, 297 and 260 kJ/mol respectively.
- 10. (a): The elements of group-14 show tetravalency by sharing four of its valence electrons. They have O.S. of +4. Ge, Sn and Pb also show +2 O.S. The stability of dihalides increases down the group. The stability of dihalides follow the sequence:

$$CX_2 << SiX_2 << GeX_2 << SnX_2 << PbX_2$$

- 11. (a, b): The chain length of the polymer can be controlled by adding Me<sub>3</sub>SiCl which blocks the ends of silicone polymer.
- 12. (a, c): In PbO<sub>2</sub>, oxidation state of Pb is +4, passes readily into more stable oxidation state +2 (due to inert pair effect) and hence, is a strong oxidising agent. On the contrary, GeCl<sub>2</sub> is a strong reducing agent.
- 13. (c, d)
- 14. (d):  $PbO_2$  is the strongest oxidising agent as it readily changes from +4 to +2 oxidation state.
- 15. (a) 16. (c)
- 17. (a): Due to  $p\pi$ - $p\pi$  back bonding, B—F bond possess some double bond character.
- 18. (b) 19. (a) 20. (a) 21. (a)
- **22.** (d): In CO<sub>2</sub> molecule, carbon atom undergoes sp hybridisation. The two sp hybridised orbitals of C-atom overlap with two p-orbitals of O-atoms to make 2  $\sigma$  bonds while other two electrons of C-atom are involved in  $p\pi$ - $p\pi$  bonding with oxygen atom. Hence, it is linear in shape with equal C—O bond lengths and no dipole moment.

$$\ddot{O} \stackrel{\text{def}}{=} C \stackrel{\text{def}}{=} \ddot{O}$$
:  $\therefore \mu = 0$ 

- 23. (0): H<sub>3</sub>BO<sub>3</sub> is not protonic acid. It is a Lewis acid as it can accept a pair of electrons from OH<sup>-</sup> ion of water.
- **24.** (1): To give branched chain silicone, the number of Cl atoms must be three to give CH<sub>3</sub>Si(OH)<sub>3</sub>, which on condensation gives branched silicone.
- 25. (2): Oxidation state of C in CO is +2

$$\therefore$$
  $x = +2$ 

Oxidation state of C in COCl<sub>2</sub> is +4

$$\therefore$$
  $y = +4$ 

Now, 
$$y - x = 4 - 2 = 2$$



CHAPTERWISE PRACTICE PAPER : THE p-block elements | Organic Chemistry-some basic principles and techniques

Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.
- 1. What is the maximum covalency of silicon in its compounds?
- **2.** Give the IUPAC name of the saturated hydrocarbon having the following carbon skeleton.

- **3.** What is inert pair effect?
- 4. How many  $\sigma$  bonds and  $\pi$  bonds are present in the second member of the alkene series?
- **5.** What is catenation?
- 6. Like CO, its analogue SiO is not stable. Why?
- 7. By mistake, an alcohol (boiling point 97°C) was mixed with a hydrocarbon (boiling point 68°C). Suggest a suitable method to separate the two compounds. Explain the reason for your choice.
- **8.** How does NaBH<sub>4</sub> react with iodine? Also discuss the structure of the main product formed.
- **9.** What are reactive intermediates? How are they generated by bond fission?

**10.** Will CCl<sub>4</sub> give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

#### OR

In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these? Give reason.

- 11. What happens when
  - (i) Borax is heated strongly
  - (ii) Boric acid is added to water
  - (iii) Aluminium is treated with HCl?
- **12.** Identify the reagents shown in brackets in the following equations as nucleophiles or electrophiles:

(a) 
$$CH_3COOH + (NH_3) \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

(b) 
$$CH_3COCH_3 + (CN^-) \longrightarrow (CH_3)_2C(CN)(OH)$$

(c) 
$$C_6H_6 + (CH_3\overset{+}{C}O) \longrightarrow C_6H_5COCH_3$$

#### OF

How many cyclic and acyclic isomers are possible for the molecular formula  $C_3H_6O$ ? Draw the structures also.

- 13. A non-metallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as Lewis acid towards ammonia. The element exhibits maximum covalency of four. Identify the element and write the reaction of its trifluoride with ammonia. Explain why does the trifluoride act as a Lewis acid.
- **14.** Explain the terms inductive and electromeric effects. Which electron displacement effect explains the following orders of acidity of the carboxylic acids?
  - (a) Cl<sub>3</sub>CCOOH > Cl<sub>2</sub>CHCOOH > ClCH<sub>2</sub>COOH
  - (b) CH<sub>3</sub>CH<sub>2</sub>COOH > (CH<sub>3</sub>)<sub>2</sub>CHCOOH

> (CH<sub>3</sub>)<sub>3</sub>CCOOH

- **15.** How will you prepare the following in steps not exceeding three (give reactions only)?
  - (i) Silicon from SiCl<sub>4</sub>
  - (ii) Linear silicon containing methyl groups only from Si
  - (iii) Hydrofluorosilicic acid from SiO<sub>2</sub>
- **16.** What is the difference between distillation, distillation under reduced pressure and steam distillation?
- **17.** Rationalise the given statements and give chemical reactions:
  - (i) Lead (II) chloride reacts with Cl<sub>2</sub> to give PbCl<sub>4</sub>.
  - (ii) Lead (IV) chloride is highly unstable towards
  - (iii) Lead is known not to form an iodide, PbI<sub>4</sub>.
- **18.** Arrange the following:
  - (i)  $C_6H_5CHCH_3$ ,  $C_6H_5CHCH = CH_2$ ,  $C_6H_5CH_2CH_2$ ,  $C_6H_5C(CH_3)_2$  in order of increasing stability.
  - (ii)  $CH_3\overset{+}{C}H_2$ ,  $C_6H_5\overset{+}{C}H_2$ ,  $(CH_3)_3\overset{+}{C}$ ,  $CH_2 = CH\overset{+}{C}H_2$  in order of decreasing stability.
  - (iii)  $HC \equiv C^-, CH_2 = CH^-, CH_3CH_2^-, CH_3^-, (CH_3)_2CH^-, C_6H_5CH_2^-$  in order of increasing stability.
- **19.** Draw the structure of boric acid showing hydrogen bonding. In which form it is present in water? What is the hybridisation of boron in this species?
- **20.** What is meant by hybridisation? Compound  $CH_2=C=CH_2$  contains sp or  $sp^2$  hybridised carbon atoms. Will it be a planar molecule?
- **21.**  $H_3O^+$  or  $R_4N^+$ neither acts as an electrophile nor as a nucleophile. Explain why.

**22.** Which of the following is not hydrolysed by water and why?

BF<sub>3</sub>, BCl<sub>3</sub> and BBr<sub>3</sub>

- 23. Students of Class XI, were given different compounds for the detection of extra elements present in the compound by their science teacher. For this, all the students prepared sodium extract and used it for detection. Pratiksha added a small amount of freshly prepared ferrous sulphate to a part of sodium extract and warmed it. She then added few drops of FeCl<sub>3</sub> and acidified the resultant solution with dil. HCl. She got a bluish green colouration. Her fellow mate, Ritwik followed the same sequence of steps as followed by Pratiksha but he got a blood red colouration. Ritwik thought he has performed the test incorrectly. Pratiksha explained him the reason for different colouration. Now, answer the following questions:
  - (a) What did Pratiksha explain him?
  - (b) Write the reactions involved in both the cases.
  - (c) What are the values shown by Pratiksha?
- **24.** Describe the general trends in the following properties of the elements in Group 13 and 14.
  - (i) Atomic size
- (ii) Ionisation enthalpy
- (iii) Metallic character
- (iv) Oxidation states
- (v) Nature of halides

#### OR

When  $BCl_3$  is treated with water, it hydrolyses and forms  $[B(OH)_4]^-$  only whereas  $AlCl_3$  in acidified aqueous solution forms  $[Al(H_2O)_6]^{3+}$  ion. Why? Explain what is the hybridisation of boron and aluminium in these species?

- **25.** Draw the resonance structures for the following compounds. Show the electron shift using curved arrow notation.
  - (i)  $C_6H_5OH$
- (ii)  $C_6H_5NO_2$
- (iii) CH<sub>3</sub>CH = CHCHO
- (iv)  $C_6H_5 CH_2$
- (v)  $CH_3CH = CHCH_2$

#### OR

Answer the following questions:

(a) Benzoic acid is an organic compound. Its crude sample can be purified by crystallisation from hot water. What characteristic differences in the properties of benzoic acid and the impurity make this process of purification suitable?

- (b) An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.
- **26.** Answer the following questions:
  - (a) Explain why BF<sub>3</sub> exists but BH<sub>3</sub> does not.
  - (b) Gallium has higher ionization enthalpy than aluminium. Why?
  - (c) AlF<sub>3</sub> is high melting solid but AlCl<sub>3</sub> is low melting. Explain.

Answer the following:

- (a) Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. A piece of aluminium foil is treated with dilute hydrochloric acid or dilute sodium hydroxide solution in a test tube and on bringing a burning matchstick near the mouth of the test tube, a pop sound indicates the evolution of hydrogen gas. The same activity when performed with concentrated nitric acid, reaction does not proceed. Explain the reason.
- **(b)** Identify the compounds A, X and Z in the following reactions:

(i) 
$$A + 2HCl + 5H_2O \longrightarrow 2NaCl + X$$

(ii) 
$$X \xrightarrow{\Delta} HBO_2 \xrightarrow{\text{Red heat}} Z$$

#### SOLUTIONS

- 1. Silicon shows maximum covalency in its compounds equal to six e.g., Na<sub>2</sub>SiF<sub>6</sub>.
- 2. 5-Ethyl-2, 3, 4-trimethyloctane
- 3. In the elements of  $4^{th}$ ,  $5^{th}$  and  $6^{th}$  period of the p-block, ns<sup>2</sup>-electrons remain more tightly held by the nucleus due to poor shielding of d- and f-electrons and hence, do not participate in bonding. This is called inert pair effect.
- The second member of the alkene series is propene. The structural formula of the propene is

H H H  

$$H - C - C = C - H$$
 Number of  $\sigma$  bond = 8  
Number of  $\pi$  bond = 1

5. Property of self-linking of atoms to form chains or rings of various sizes is called catenation. Carbon

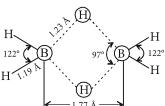
has the maximum tendency for catenation due to high bond strength of C—C bonds.

CO has the following resonating structures :  $: C \stackrel{\checkmark}{=} \stackrel{\cdot}{O} : \longleftrightarrow : C \stackrel{+}{=} \stackrel{+}{O} :$ 

Therefore, CO has  $p\pi$ - $p\pi$  multiple bonds. This is because C being small in size and having high electronegativity than Si forms strong  $p\pi$ - $p\pi$  bond. Silicon on the otherhand, because of its larger size and lower electronegativity has no tendency to form  $p\pi$ - $p\pi$  bond and hence, does not form stable SiO.

- The difference in boiling points of two liquids is more than 25°C. Hence, simple distillation can be used and since at the boiling point of low boiling liquid, the vapours would consist entirely of only low boiling liquid without any contamination of vapours of high boiling liquid and vice-versa. Thus, both the liquids can be distilled without any decomposition.
- When NaBH<sub>4</sub> reacts with iodine diborane is produced:

 $2\text{NaBH}_4 + \text{I}_2 \xrightarrow{\text{Diglyme}} \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$ In the structure of diborane four hydrogen atoms, two on the left and two on the right, known as terminal hydrogens and two boron atoms lie in the same plane. Two hydrogen atoms forming bridges, one above and other below, lie in a plane perpendicular to the rest of molecule.



Reactive intermediates are short-lived, high-energy, highly reactive molecules generated in a chemical reaction. These molecules quickly convert into a more stable product e.g., carbocation, carbanion and free radical etc. Carbocation and carbanion are generated by the heterolytic bond fission while free radical is produced by homolytic bond fission.

$$CH_3$$
  $Cl$   $\longrightarrow$   $CH_3^+ + Cl^-$   
 $(CH_3)_2Zn$   $\longrightarrow$   $2CH_3^- + Zn^{2+}$   
(Heterolytic bond fission)  
 $CH_3$   $CH_3$   $\longrightarrow$   $2CH_3^*$   
(Homolytic bond fission)

10. No. AgNO<sub>3</sub> solution is ionic in nature. It contains Ag<sup>+</sup> ion which when reacts with Cl<sup>-</sup> ions, produces a white ppt. of AgCl. While CCl<sub>4</sub> is a covalent compound and does not produce Cl<sup>-</sup> ions. Therefore, when AgNO<sub>3</sub> is added to it, it does not produce a white ppt. of AgCl.

#### OR

Nitrogen atom present in DNA and RNA cannot be estimated by Kjeldahl method. DNA and RNA have nitrogen in the heterocyclic rings. Nitrogen present in rings, azo and nitro groups cannot be converted into ammonium sulphate. Thus, Kjeldahl method cannot be used for the estimation of nitrogen present in DNA and RNA.

11. (i) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid which solidifies into glass like material called borax bead.

$$\begin{array}{c} Na_2B_4O_7.10H_2O \xrightarrow{Heat} Na_2B_4O_7 \xrightarrow{Heat} \\ Borax & Anhydrous \\ & 2NaBO_2 + B_2O_3 \\ Sodium & Boric \\ metaborate & anhydride \end{array}$$

- (ii) It acts as Lewis acid by accepting electrons from a hydroxyl ion.
   B(OH)<sub>3</sub> + H<sub>2</sub>O → [B(OH)<sub>4</sub>]<sup>-</sup> + H<sup>+</sup>
   Boric acid
- (iii) Hydrogen gas is liberated.  $2Al + 6HCl \longrightarrow 2Al^{3+} + 6Cl^{-} + 3H_{2}$

12. (a) 
$$H_3C - C + NH_3 \xrightarrow{O} H_3C - C + NH_2$$

Here, NH<sub>3</sub> is acting as a nucleophile.

(b) 
$$H_3C$$
  $CH_3$   $CN$   $H_3C$   $CN$   $CN$ 

Here, CN<sup>-</sup> is acting as a nucleophile. The carbonyl carbon is a positive centre, since the oxygen withdraws the carbonyl electron and leaves the carbon atom electron deficient.

(c) 
$$+CH_3-C$$
  $\longrightarrow$   $+CCH_3$ 

CH<sub>3</sub>CO<sup>+</sup> is an electrophile. Benzene being an electron rich molecule, is most suitable for an electrophilic attack.

#### OR

Seven following isomers are possible:

- (a) Acyclic isomers:
- (i) CH<sub>3</sub>CH<sub>2</sub>CHO Propanal

(ii) 
$$CH_3 - C - CH_3$$
Acetone

- (iii)  $CH_2 = CHCH_2OH$ Prop-2-en-1-ol
- (iv)  $CH_2 = CHOCH_3$ Methoxyethene
- **(b)** Cyclic isomers:

13. The only non-metallic element of group 13 is boron. It is an extremely hard black substance and is used in making bullet proof vests. It exists in many allotropic forms and has unusually high melting point. Since B does not have vacant *d*-orbitals, therefore, it can exhibit maximum covalency of four.

$$H_3N + BF_3 \longrightarrow H_3N \longrightarrow BF_3$$

Since B in BF<sub>3</sub> has only six electrons in its valence shell, therefore, it needs two more electrons to complete its octet. Thus, BF<sub>3</sub> acts as a Lewis acid.

- 14. Inductive effect: Polarisation of  $\sigma$ -bond due to the electron donating or withdrawing nature of groups attached is called inductive effect.
  - e.g. Attachment of Cl, an electronegative atom to an ethane molecule causes the carbons to carry a  $\delta^+$  charge.

$$Cl \leftarrow CH_2 \leftarrow CH_3$$

Electromeric effect: In the presence of an attacking reagent, the  $\pi$ -electron cloud in a multiple bonded compound tends to get polarized. Such an effect is termed as temporary effect and the original condition is restored if the reagent is removed.

$$+ H^{+} \longrightarrow + H$$
or
$$+ CN \longrightarrow - CN$$

- (a) The given order of acidity can be explained by −I effect of chlorine atom. More the no. of Cl atoms, higher is the acidic strength. Cl<sub>3</sub>CCOOH > Cl<sub>2</sub>CHCOOH > ClCH<sub>2</sub>COOH
- **(b)** The given order of acidity can be explained by +I effect of  $-CH_3$  group. More the number of -CH<sub>3</sub> groups on the  $\alpha$ -carbon, lower will be the acidic strength.

15. (i) 
$$\operatorname{SiCl}_4 + 2H_2 \xrightarrow{\Delta} \operatorname{Si} + 4HCl$$

(ii) 
$$Si + 2CH_3Cl \xrightarrow{Cu \text{ powder}} (CH_3)_2SiCl_2 \xrightarrow{CH_3} (CH_3)_2SiCl_2 \xrightarrow{HOH} HO \xrightarrow{CH_3} OH CH_3$$

$$n(CH_3)_2Si(OH)_2 \xrightarrow{\text{Heat}}$$

$$CH_3 \quad CH_3 \quad CH_3$$

$$-Si - O - Si - O - Si - O -$$

$$CH_3 \quad CH_3 \quad CH_3$$

$$-CH_3 \quad CH_3 \quad CH_3$$

(iii)  $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$ SiF<sub>4</sub> thus formed dissolves in HF to form hydrofluorosilicic acid.

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

Hydrofluoro silicic acid

16. Differences between distillation, distillation under reduced pressure and steam distillation may be summarized

Criterion for difference	Distillation	Distillation under reduced pressure	Steam distillation
Used for	Separation of volatile liquids from non-volatile impurities and the liquids having sufficient difference in their boiling points.	Purify liquids having very high boiling points or those, which decompose at or below their boiling points.	are immiscible with water
Method	Simple heating of the mixture in a round bottom flask fitted with condenser allows the lower boiling liquid to be collected first and the higher boiling one is collected later.	Since, one of the component decomposes before reaching its boiling point the heating is carried out under reduced pressure so that boiling occurs at a lower temperature and the component is collected in pure form.	volatile organic compound is condensed and collected. The compound is later separated from water using a separating
Example	A mixture of chloroform (b.pt. 334 K) and aniline (b.pt. 457 K).	Separation of glycerol from spent - lye in soap industry.	Separation of aniline from aniline-water mixture.

- 17. (i)  $PbCl_2 + Cl_2 \longrightarrow PbCl_4$ Lead is more stable in +2 oxidation state than in +4 state due to inert pair effect. Thus, the reaction is not feasible.
  - (ii)  $PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$ Pb is more stable in its +2 oxidation state due to inert pair effect. As a result, when subjected to heat, Pb (IV) goes to Pb (II) state.
  - (iii)  $Pb + 2I_2 \longrightarrow PbI_4$ I is a good reducing agent and therefore,

reduces Pb (IV) to Pb (II) easily. That is why, PbI₄ does not exist.

18. (i) 
$$C_6H_5CH_2\overset{+}{C}H_2 < C_6H_5\overset{+}{C}HCH_3 < C_6H_5\overset{+}{C}(CH_3)_2$$
  
 $< C_6H_5\overset{+}{C}HCH = CH_2$ 

(ii) 
$$C_6H_5\overset{+}{C}H_2 > CH_2 = CH\overset{+}{C}H_2 > (CH_3)_3\overset{+}{C} > CH_3\overset{+}{C}H_2$$

(iii) 
$$(CH_3)_2CH^- < CH_3CH_2^- < CH_3^- < CH_2 = CH^-$$
  
 $< HC \equiv C^- < C_6H_5CH_2^-$ 

19. Boric acid has a layer structure in which planar BO<sub>3</sub> units are joined by hydrogen bonds.

Structure of boric acid; the dotted lines represent hydrogen bonds

It is present in water as [B(OH)<sub>4</sub>] unit. Boron has  $sp^3$  hybridisation in  $[B(OH)_4]^-$  unit.

20. Intermixing of atomic orbitals of same atom with slightly different energies resulting in the formation of same number of new orbitals with equal energies and shape is known as hybridisation.

Central carbon atom is sp hybridised and its two unhybridised p-orbitals are perpendicular to each other. The *p*-orbitals in one plane overlap with one of the p-orbitals of left terminal carbon atom and the *p*-orbital in other plane overlaps with *p*-orbital of right side terminal carbon atom. As a result the position of two terminal carbon atoms and the hydrogen atoms attached to them are fixed in planes perpendicular to each other. Therefore, the pair of hydrogen atoms attached to terminal carbon atoms are present in different planes and hence molecule is not planar.

21.  $H_3O^+$  has a lone pair of electrons but due to the presence of +ve charge, it cannot donate its electron pair and hence it does not act as a nucleophile.  $R_4N^+$ , however, does not have a lone pair of electrons, therefore, it does not act as a nucleophile. H<sub>3</sub>O<sup>+</sup> has 8 electrons in the valence shell. It cannot expand its valence shell beyond 8 due to the absence of d-orbitals. Therefore, it does not act as an electrophile. Similarly,  $R_4N^+$  also has 8 electrons in the valence shell. Like O, N also cannot expand

its valence shell beyond 8 and hence it also does not act as an electrophile.

Thus,  $H_3O^+$  or  $R_4N^+$  neither acts as a nucleophile nor as an electrophile.

22. BF<sub>3</sub> is not easily hydrolysed by water. It forms an hydrolysed to boric acid and HCl or HBr respectively. This is because the B - F bond in  $BF_3$  is very strong due to extensive  $p\pi$ - $p\pi$  back bonding. As a result, it is not hydrolysed by water. The B - F bond energy is far larger than B — OH bond energy and cannot be compensated.

$$F - B \stackrel{F}{\searrow} + H_2O \xrightarrow{\longrightarrow} HO - B \stackrel{OH}{\searrow} + 3HF$$

However, in BCl<sub>3</sub> and BBr<sub>3</sub>, the corresponding B — Cl and B — Br bond energy is relatively less than B – F because of inefficient  $p\pi$ - $p\pi$  back bonding. Therefore, these get hydrolysed.

23. (a) Pratiksha explained Ritwik that he has performed the experiment correctly. The compound she got contained only nitrogen whereas Ritwik's compound had both nitrogen and sulphur.

(b) Na + 
$$\underbrace{C+N}$$
  $\longrightarrow$  NaCN

From organic compound

$$\begin{aligned} & \text{FeSO}_4 + 2 \text{NaCN} & \longrightarrow \text{Fe}(\text{CN})_2 + \text{Na}_2 \text{SO}_4 \\ & \text{Fe}(\text{CN})_2 + 4 \text{NaCN} & \longrightarrow \text{Na}_4 [\text{Fe}(\text{CN})_6] \end{aligned}$$

Sodium hexacyanoferrate (II)

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \xrightarrow{xH_2O}$$

$$Fe_4[Fe(CN)_6]_3.xH_2O + 12NaCl$$
(Prussian blue)

In second case:

Na + 
$$C + N + S$$
  $\xrightarrow{\Delta}$  NaSCN

From organic Sodium thiocyanate

3NaSCN + FeCl<sub>3</sub>  $\longrightarrow$  Fe(CNS)<sub>3</sub> + 3NaCl

Ferric thiocyanate (Blood red)

- Knowledge and teaching aptitude are the values shown by Pratiksha.
- 24. (i) Atomic size: Atomic radii of group 13 elements increase down the group with exception Ga < Al due to presence of extra ten d-electrons which offer poor screening effect. In group 14, there is a considerable

increase in radius from C to Si, thereafter from  $Si \rightarrow Pb$  a small increase is seen due to presence of completely filled *d*- and *f*- orbitals.

- (ii) Ionisation enthalpy: For group 13, the trend is B > Al < Ga > In < Tl. This is due to increase in size and low screening effect of *d*- and *f*- electrons.
  - Group 14 elements have higher I.E. than group 13 elements. First I.E. decreases from C to Sn. The exceptions of increase in I.E. from  $Sn \rightarrow Pb$  is due to poor shielding effect of *d*- and *f*- orbitals.
- (iii) Metallic character : Metallic character increases from boron to aluminium then decreases down the group for group 13 elements. Due to smaller size group 14 elements are less metallic. Metallic character increases gradually down the group. C (nonmetal), Si, Ge (metalloid) Sn, Pb (metal).
- (iv) Oxidation states: For group 13 both +1 and +3 oxidation states are observed. +1 oxidation state becomes more stable as we move down the group due to inert pair effect. Boron does not show +3 oxidation states.
  - For group 14 common oxidation states are +4 and +2. Tendency to show +2 oxidation state increases down the group.
- (v) Nature of halides: Group 13 elements form trihalides (except TlI<sub>3</sub>). Due to electron deficient nature BCl3 accepts electrons and forms adduct. AlCl<sub>3</sub> achieves stability by forming a dimer. Group 14 elements form halides with formula  $MX_2$  and  $MX_4$ . Except CCl<sub>4</sub> other halides are easily hydrolysed. Stability of dihalides increases down the group.

#### OR

When BCl<sub>3</sub> reacts with water, it first undergoes hydrolysis to form boric acid, B(OH)3. Due to small size and high electronegativity of B, B(OH)<sub>3</sub> polarizes H<sub>2</sub>O molecule accepting an OH<sup>-</sup> ion to form  $[B(OH)_4]^-$  species and releasing a proton.

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$

$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

Since B lies in the 2<sup>nd</sup> period, it has only one s- and three p-orbitals but no d-orbitals. In other words, at the maximum, it can have four pairs of electrons in the valence shell, i.e., its maximum coordination number is 4. That is why, it accepts one OH ion forming [B(OH)<sub>4</sub>] in which boron

is sp<sup>3</sup>-hybridized. In contrast, AlCl<sub>3</sub>, undergoes hydrolysis in acidified aqueous solution to form  $[Al(H_2O)_6]^{3+}$ 

$$AlCl_3 + 6H_2O \xrightarrow{HCl} [Al(H_2O)_6]^{3+} + 3Cl_{(aq)}^{-}$$

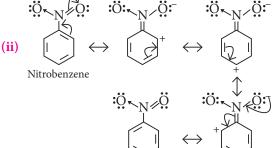
This may be explained as follows: (i) In acidic medium, the conc. of OH<sup>-</sup> ions is much lower than that of H<sup>+</sup> ions, therefore, Al<sup>3+</sup> ions coordinate with H<sub>2</sub>O molecules and not with OH<sup>-</sup> ions.

(ii) Due to the presence of vacant d-orbitals in Al<sup>3+</sup> ions, it can expand its coordination number from 4 to 6 and hence forms  $[Al(H_2O)_6]^{3+}$  in which hybridization of Al is  $sp^3d^2$ .

E.C. of Al :  $[Ne]3s^23p^1$ 

E.C. of 
$$Al^{3+}$$
: [Ne]  $3b$   $3d$ 

Formation of  $Al(H_2O)_6$ ]<sup>3+</sup>



#### **ANSWER MPP-8 CLASS XI**

- (d) (d) **1.** (b) **5.** (a)
- (c) **6.** (c) (d) **10.** (d)
- **11.** (c) **12.** (c) 13. (b) **14.** (a) **15.** (c)
- **16.** (a) 18. (d) **17.** (d) **19.** (b) **20.** (b,c)
- **21.** (a,b,c) **22.** (a,b,c,d) **23.** (b,d) **24.** (3) **25.** (6)

(iii) 
$$CH_3-CH=CH-CH=\overset{\bullet}{O}$$
:
$$But-2-en-1-al \overset{\bullet}{\downarrow}$$

$$CH_3-CH=\overset{\bullet}{CH}\overset{\bullet}{\to}\overset{\bullet}{CH}-\overset{\bullet}{O}$$
:
$$CH_3-\overset{\dagger}{CH}-CH=CH-\overset{\bullet}{O}$$
:
$$\overset{\dagger}{CH_2}$$

$$CH_2 \overset{\bullet}{\to}\overset{\bullet}{\to}$$

$$CH_3-CH=CH=CH_2 \overset{\bullet}{\to}$$

$$CH_3-\overset{\bullet}{C}H-CH=CH_2 \overset{\bullet}{\to}$$

$$CH_3-\overset{\bullet}{C}H-CH=CH_2 \overset{\bullet}{\to}$$

- (a) Benzoic acid can be purified by hot water because of the following characteristics:
  - (i) Benzoic acid is more soluble in hot water and less soluble in cold water.
  - (ii) Impurities present in benzoic acid are either insoluble in water or are more soluble in water to such an extent that they remain in solution as the mother liquor upon crystallisation.

(b) % C = 
$$\frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$69 = \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{0.2} \times 100$$

:. Mass of CO<sub>2</sub> formed

$$= \frac{69 \times 44 \times 0.2}{12 \times 100} = 0.506 \text{ g}$$

% H = 
$$\frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of substance taken}} \times 100$$

$$4.8 = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{0.2} \times 100$$

 $\therefore$  Mass of H<sub>2</sub>O formed

$$= \frac{4.8 \times 18 \times 0.2}{2 \times 100} = 0.0864 \text{ g}$$

**26.** (a) In BF<sub>3</sub>, the vacant 2p-orbital of boron accepts  $\pi$  electron density by overlapping with filled  $2p_z$  orbital of F. Therefore, the stability of BF<sub>3</sub> is due to back bonding.

However, hydrogen atoms do not have free electrons to form back bonding with boron and therefore,  $BH_3$  is not stable. However, to satisfy the electron deficiency of boron, it dimerizes to form  $B_2H_6$ .

- (b) Gallium has higher ionization enthalpy than aluminium because of higher effective nuclear charge. This is due to additional ten *d*-electrons which do not shield the nuclear charge effectively so that the outer electrons are strongly held.
- (c) AlF<sub>3</sub> is high melting solid because it is ionic in nature. On the other hand, AlCl<sub>3</sub> is covalent in nature and hence is a low melting solid.

#### OR

(a) Al being amphoteric dissolves both in acids and alkalies evolving H<sub>2</sub> gas which burns with a pop sound.

$$2\text{Al} + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2$$
  
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$   
(Sod. metaaluminate)

With conc. HNO<sub>3</sub>, Al becomes passive and the reaction does not proceed. This passivity is due to the formation of a thin protective layer of its oxide ( $Al_2O_3$ ) on the surface of the metal which prevents further action.

$$2Al_{(s)} + 6HNO_3 \longrightarrow Al_2O_{3(s)} + 6NO_{2(g)} + 3H_2O_{(l)}$$

(b) (i) 
$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl$$
  
 $Borax(A) + 4H_3BO_3$ 

Boric acid (X)

(ii) 
$$H_3BO_3 \xrightarrow{\Delta, >370 \text{ K}} HBO_2 + H_2O$$
  
 $(X) \xrightarrow{-H_2O} Metaboric acid$ 

$$4HBO_2 \xrightarrow{410 \text{ K (Red heat)}} 2B_2O_3$$
Boron trioxide (Z)

## MPP-8 MONTHLY Practice Problems

This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.



## The p-Block Elements

Total Marks: 120 Time Taken: 60 Min.

#### NEET / AIIMS

#### **Only One Option Correct Type**

- 1. 2 g of aluminium is treated separately with excess of dilute H<sub>2</sub>SO<sub>4</sub> and excess of NaOH. The ratio of the volumes of hydrogen evolved is
  - (a) 2:3
- (b) 1:1
- (c) 2:1
- (d) 1:2
- **2.** First ionisation enthalpy for the elements of group-13 follows the order
  - (a) B > Al > Ga > In > Tl
  - (b) B < Al < Ga < In < Tl
  - (c) B < Al > Ga < In > Tl
  - (d) B > Al < Ga > In < Tl
- **3.** The stability of +1 oxidation state increases in the sequence
  - (a) Tl < ln < Ga < Al (b) ln < Tl < Ga < Al
  - (c) Ga < ln < Al < Tl
- (d) Al < Ga < ln < Tl
- **4.** Boron cannot form which one of the following anions?
  - (a)  $BF_6^{3-}$
- (b) BH<sub>4</sub>
- (c)  $B(OH)_{4}^{-}$
- (d)  $BO_2$
- **5.** Which is not correct?
  - (a) GeCl<sub>2</sub> is more stable than GeCl<sub>4</sub>.
  - (b) Ge(OH)<sub>2</sub> is amphoteric.
  - (c)  $GeO_2$  is weakly acidic.
  - (d) GeCl<sub>4</sub> in HCl forms [GeCl<sub>2</sub>]<sup>2-</sup> ion.
- **6.** Graphite is a soft solid lubricant extremely difficult to melt because graphite
  - (a) is an allotropic form of carbon
  - (b) is a non-crystalline substance
  - (c) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds

- (d) has molecules of variable molecular masses like polymers.
- The transformation of metallic tin into grey powder is due to
  - (a) the interaction with nitrogen of the air at very low temperature
  - (b) the interaction with water vapour contained in the humid air
  - (c) a change in the partial pressure of oxygen in air
  - (d) a change in the crystalline structure of tin.
- **8.** Which of the following is incorrect for the fact, 'carbon differs from other elements of the group'?
  - (a) It has significant tendency to form long chains.
  - (b) It has unique ability to form multiple bonds.
  - (c) It has *d*-orbital in penultimate shell.
  - (d) Maximum coordination number of carbon is 4.
- 9. In aluminium extraction by the Baeyer's process, alumina is extracted from bauxite by sodium hydroxide at high temperature and pressure.  $Al_2O_{3(s)} + 2OH_{(aq)}^- \longrightarrow 2AlO_{2(aq)}^- + H_2O_{(l)}$  Solid impurities such as  $Fe_2O_3$  and  $SiO_2$  are removed and then  $Al(OH)_4^-$  is reprecipitated.  $2Al(OH)_4^- \longrightarrow Al_2O_3$ .  $3H_2O + 2OH^-$ 
  - In the industrial world
  - (a) carbon dioxide is added to precipitate the alumina
  - (b) temperature and pressure are dropped and the supersaturated solution is seeded
  - (c) both (a) and (b) are practised
  - (d) water is evaporated.
- **10.** In diborane, the number of electrons that account for bonding in the bridges is
  - (a) six
- (b) two
- (c) eight
- (d) four.

- **11.** Which of the following statements is incorrect with respect to the structure of diborane?
  - (a) There are four terminal hydrogen atoms and two bridged hydrogen atoms.
  - (b) The terminal hydrogen atoms and boron atoms lie in a plane.
  - (c) There are five two-centred and five three-centred bonds.
  - (d) Two bridged hydrogen atoms lie above and below the plane.
- 12. What is not true about borax?
  - (a) Molecular formula is  $Na_2B_4O_7.10H_2O$ .
  - (b) Crystalline borax contains tetranuclear units of  $[B_4O_5(OH)_4]^{2-}$ .
  - (c) It hydrolyses to give an acidic solution.
  - (d) It is a white crystalline solid.

#### **Assertion & Reason Type**

**Directions :** In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- **13. Assertion :** Silicones are water repelling in nature. **Reason :** Silicones are organosilicon polymers, which have  $(R_2SiO-)$  as repeating unit.
- **14. Assertion :** Borazole is aromatic in nature. **Reason :** Nitrogen contributes  $\pi$ -electrons t

**Reason :** Nitrogen contributes  $\pi$ -electrons to the system.

**15. Assertion :** Molten AlBr<sub>3</sub> is poor conductor of electricity.

**Reason**: AlBr<sub>3</sub> being ionic in nature provides Al<sup>3+</sup> and Br<sup>-</sup> ions.

#### **JEE MAIN / JEE ADVANCED**

#### **Only One Option Correct Type**

**16.** Diborane, B<sub>2</sub>H<sub>6</sub>, reacts with water to form boric acid and hydrogen. What is the pH of the solution which results when 1.104 g of B<sub>2</sub>H<sub>6</sub> reacts with 100 mL water? Assume the final volume to be 100 mL.

(Given :  $K_a$  of  $H_3BO_3 = 8 \times 10^{-10}$ ,  $pK_a = 9.1$ )

- (a) 4.6
- (b) 6.2
- (c) 8.9
- (d) 7.2

- 17. Which one of the following is the correct statement?
  - (a)  $B_2H_6 \cdot 2NH_3$  is known as 'inorganic benzene'.
  - (b) Boric acid is a protonic acid.
  - (c) Beryllium exhibits coordination number six.
  - (d) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase.
- 18. X reacts with NaOH (aqueous solution) to form Y and H<sub>2</sub>. Aqueous solution of Y is heated to 323-333 K and on passing CO<sub>2</sub> into it, Na<sub>2</sub>CO<sub>3</sub> and Z are formed. When Z is heated to 1200 °C, Al<sub>2</sub>O<sub>3</sub> is formed. X, Y and Z respectively are
  - (a) Al, AlCl<sub>3</sub>, NaAlO<sub>2</sub>
  - (b) Zn,  $Na_2ZnO_2$ ,  $Al(OH)_3$
  - (c) Al, Al(OH)<sub>3</sub>, AlCl<sub>3</sub> (d) Al, NaAlO<sub>2</sub>, Al(OH)<sub>3</sub>
- 19.  $NH_3 + CO_2 \xrightarrow{pressure/\Delta} X \xrightarrow{\Delta} Y$

X and Y are respectively

- (a) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>2</sub>COONH<sub>4</sub>
- (b)  $NH_2COONH_4$ ,  $NH_2-CO-NH_2$
- (c)  $NH_2COOH$ ,  $NH_2-CO-NH_2$
- (d)  $(NH_4)_2CO_3$ ,  $NH_2 CO NH_2$

#### More than One Options Correct Type

- 20. Which of the following statements are correct?
  - (a) Fullerenes have dangling bonds.
  - (b) Fullerenes are cage-like molecules.
  - (c) Graphite is thermodynamically most stable allotrope of carbon.
  - (d) Graphite is slippery and hard and therefore used as a dry lubricant in machines.
- **21.** In the following reaction,

$$2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$$
  
X can be

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- (a) NH<sub>3</sub>
- (b) CH<sub>3</sub>NH<sub>2</sub>
- (c) (CH<sub>3</sub>)<sub>2</sub>NH
- (d) (CH<sub>3</sub>)<sub>3</sub>N
- **22.** Select the correct statements.
  - (a) Borax is used as a buffer.
  - (b) 1 M borax solution reacts with equal volumes of 2 M HCl solution.
  - (c) A solution of borax can be titrated with a mineral acid using methyl orange as indicator.
  - (d) Coloured bead obtained in borax bead test contains metaborate.
- 23. Select the correct statements about silicates.
  - (a) Cyclic silicate having three Si atoms contains six Si - O - Si linkages.
  - (b) Chain silicates contain  $(SiO_3)_n^{2n-}$  ions which are formed by linking  $SiO_4^{4-}$  uints linearly.
  - (c)  $(Si_2O_5)_n^{2n-}$  is the formula of double chain silicate.
  - (d)  $SiO_4^{4-}$  units polymerize to form silicate because Si atom has less tendency to form  $\pi$ -bond with oxygen.

#### **Integer Answer Type**

- 24. How many moles of NO<sub>2</sub> are produced when one mole of B reacts with HNO<sub>3</sub>?
- 25. The coordination number of Al in the crystalline state of AlCl<sub>3</sub> is
- **26.** How many silicon atoms are present in the anion of a pyrosilicate?

#### **Comprehension Type**

Boron is the first member of group 13 of the periodic table and is the only non-metal of this group. It has a small size, high ionization enthalpy and high electronegativity due to which it cannot lose its valence electrons to form B3+ ions. Instead, it can form three covalent bonds by sharing its three valence electrons. Consequently, boron compounds, especially the hydrides and halides are electron deficient and behave as Lewis acids.

- 27. The compound which is not a Lewis acid is
  - (a) BF<sub>3</sub>
- (b) AlCl<sub>3</sub>
- (c) BeCl<sub>2</sub>. 2H<sub>2</sub>O
- (d) SnCl<sub>4</sub>
- 28. If a molecule of  $MX_3$  has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are
  - (a) pure p
- (b) sp-hybrid
- (c)  $sp^2$ -hybrid
- (d)  $sp^3$ -hybrid.

#### **Matrix Match Type**

29. Match the Column I with Column II and choose the correct answer using the codes given below.

#### Column II Column I

- Does not show inert pair effect 1. InCl
- Q. Shows  $p\pi p\pi$  back Al 2. bonding
- R. Shows disproportionation  $N(SiH_3)_3$ reaction
- BF<sub>3</sub> Shows  $p\pi - d\pi$  back bonding

#### S R

- (a) 4 3 2
- 2 3 (b) 1
- 3 (c) 2 4 1
- (d) 4 1 2 3
- 30. Match the species given in Column I with the properties mentioned in Column II and choose the correct answer using the codes given below.

#### Column I Column II

- (P) BF<sub>4</sub>
- 1. Strong oxidising agent

- (Q) AlCl<sub>3</sub>
- 2. Lewis acid
- (R) SnO
- Can be further oxidised
- (S) PbO<sub>2</sub>
- Tetrahedral shape

#### S R

- 4 2 (a) 4 1
- 1 (b) 4 2 3
- (c) 1 4 2 3
- (d) 3 2

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No. of questions correct Marks scored in percentage

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< 60%

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## **Mechanistic Approach to Some Name Reactions**

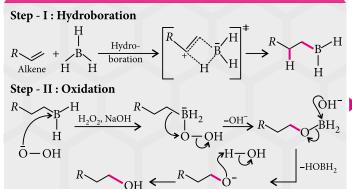
A mechanistic approach to any reaction classifies the reaction according to mechanism rather than by functional group. It explains the stereochemistry involved in a particular reaction, which can either be regioselective, stereoselective or stereospecific.

### The f-Block Elements

These elements are also called rare earth metals due to their extremely low natural occurrence. Mostly, these are prepared artificially in laboratory. All the actinoids are radioactive hence, can be used in nuclear power plants or as weapons.



## **Hydroboration – Oxidation Reaction**



- Rate of formation of the C—B bond > Rate of formation of C—H bond.
- Formation of four-centred transition state.
- Hydroboration is regioselective.
- Hydroboration is a *syn*-addition across the alkene.
- In step-II, boron goes backward and forward between planar neutral structure and anionic tetrahedral structure.
- In step-II, cleavage of O—O single bond is the driving force.
- In step-I, new C—B bond and in step-II new C—O bond are formed.
- The net result of this reaction is addition of water across the double bond.

#### Oxymercuration – Demercuration Reaction

Step - I : Oxymercuration

$$R \xrightarrow{+} Hg \xrightarrow{OAc} \xrightarrow{-AcO^{-}} R \xrightarrow{+} Hg \xrightarrow{+} Hg \xrightarrow{-H^{+}} HgOAc$$
 $R \xrightarrow{+} Hg \xrightarrow{OAc} \xrightarrow{-AcO^{-}} R \xrightarrow{+} HgOAc$ 

Step - II: Demercuration

$$R \xrightarrow{OH} HgOAc \xrightarrow{NaBH_4} R \xrightarrow{OH} H$$
Alcohol

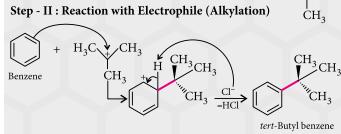
- In step-I, i.e., oxymercuration, —OH and Hg<sup>2+</sup> are added across the alkene.
- Stereochemically, oxymercuration is an anti-addition.
- In step-I, water attacks at the more substituted end of the mercurinium ion (transition state).
- Driving force for demercuration is a weak C—Hg bond.
- To replace Hg with H, NaBH<sub>4</sub>, a reducing agent is used.
- Oxymercuration-reduction is a popular laboratory technique with Markovnikov selectivity while avoiding carbocation intermediate and thus, rearrangement which can lead to complex product mixture.

## • Oxymercuration is regioselective and stereospecific.

#### Friedel-Crafts Alkylation Reaction

#### **Step - I : Formation of Intermediate (Carbocation)**

$$H_3C$$
 $CH_3$ 
 $H_3C$ 
 $CH_3$ 
 $H_3C$ 
 $CH_3$ 
 $H_3C$ 
 $CH_3$ 
 $H_3C$ 
 $CH_3$ 
 $CH_3$ 



- This reaction follows S<sub>N</sub>1 pathway.
- Species having capability to form carbocation are used.
- Carbocation can be generated by
- protonation of an alkene.
- the acid-catalysed decomposition of a tertiary alcohol.
- Lewis acid catalysed decomposition of a tert-alkyl chloride.
- Carbocation rearrangement (to more stable carbocation) takes place whenever possible.
- Friedel—Crafts alkylation with alkyl halides proceeds via a carbocation and chiral alkyl halides are expected to give racemic arene products. The extent of racemisation depends on the Lewis acid and the reaction conditions.

#### Lanthanoids (4f-series)

La	57	[Xe] $5d^1 6s^2$	Gd	64	[Xe] $4f^7 5d^1 6s^2$
Ce	58	[Xe] $4f^1 5d^1 6s^2$	Tb	65	[Xe] $4f^9 6s^2$
Pr	59	[Xe] $4f^3 6s^2$	Dy	66	[Xe] $4f^{10} 6s^2$
	60	[Xe] $4f^4 6s^2$	Но	67	[Xe] $4f^{11} 6s^2$
Nd	00		Er	68	[Xe] $4f^{12} 6s^2$
Pm	61	[Xe] $4f^5 6s^2$	Tm	69	[Xe] $4f^{13} 6s^2$
Sm	62	[Xe] $4f^6 6s^2$	Yb	70	[Xe] $4f^{14}6s^2$
Eu	63	[Xe] $4f^7 6s^2$	Lu	71	[Xe] $4f^{14} 5d^1 6s^2$

#### **Oxidation States**

+3, e.g., Gd<sup>3+</sup>, Lu<sup>3+</sup> and +2 and +4. e.g., Eu<sup>2+</sup>, Ce<sup>4+</sup> Lanthanoids show limited number of oxidation states because the energy gap between 4f- and 5d-subshells is large.

#### **Lanthanoid Contraction**

The steady decrease in the atomic/ionic radii of lanthanoids with increasing atomic no. is called *lanthanoid contraction*.

#### Cause of Lanthanoid Contraction

As the atomic number increases in lanthanoid series, the new electron goes to fill 4f-orbitals. The nuclear charge, however, increases by one at each step. Thus, there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently, the attraction of the nucleus for the electrons in the outermost shell increases which results in gradual decrease in size of lanthanoids with increase in atomic number.

#### Consequences of Lanthanoid Contraction

- Similarity in properties of second and third transition series elements.
- Due to lanthanoid contraction, the differences in physical properties enable the separation of individual lanthanoid elements by ion exchange method.
- Due to lanthanoid contraction the basic strength decreases from La(OH)<sub>3</sub> to Lu(OH)<sub>3</sub>.

#### **Magnetic Properties**

All the lanthanoid ions except La<sup>3+</sup>, Lu<sup>3+</sup>, Ce<sup>4+</sup> and Yb<sup>2+</sup> are paramagnetic. Magnetic moment ( $\mu$ ) =  $\sqrt{4S(S+1) + L(L+1)}$ 

- Used for the production of alloys e.g., Mischmetal, which contains lanthanoid metals ( $\approx$ 95%) and iron ( $\approx$ 5%).
- La<sub>2</sub>O<sub>3</sub> is used in Crooke's lenses.

### Actinoids (5f-series)

Ac	89	$[Rn] 6d^1 7s^2$	Cm	96	[Rn] $5f^7 6d^1 7s^2$
Th	90	[Rn] $6d^27s^2$	Bk	97	[Rn] $5f^97s^2$
Pa	91	[Rn] $5f^2 6d^1 7s^2$	Cf	98	[Rn] $5f^{10}7s^2$
			Es	99	[Rn] $5f^{11}7s^2$
U	92	[Rn] $5f^3 6d^1 7s^2$	Fm	100	[Rn] $5f^{12}7s^2$
Np	93	$[Rn] 5f^4 6d^1 7s^2$	Md	101	[Rn] $5f^{13}7s^2$
Pu	94	$[Rn] 5f^6 7s^2$	No	102	$[Rn] 5 f^{14} 7 s^2$
Am	95	[Rn] $5f^77s^2$	Lr	103	[Rn] $5f^{14}6d^17s^2$

#### **Oxidation States**

- General oxidation state is +3.
- Besides +3 state, other possible oxidation states are +2, +4, +5, +6 and +7.
- Actinoids show a large number of oxidation states because of very small energy gap between 5f, 6d and 7s subshells.

#### **Actinoid Contraction**

The steady decrease in ionic radii with increase in atomic number is referred to as actinoid contraction. The contraction is greater from element to element in actinoid series as compared to lanthanoid contraction. This is due to poor shielding of 5*f*-electrons.

#### Colour of the lons

The actinoid cations are generally coloured due to f-f transition, e.g.,  $U^{3+}$  (5 $f^{3}$ ): Red,  $Np^{3+}$  (5 $f^{4}$ ): Purple,  $Pu^{3+}(5f^5)$ : Violet,  $Am^{3+}(5f^6)$ : Pink,  $U^{4+}(5f^2)$ : Pink.

#### **Magnetic Properties**

The actinoid elements or ions are paramagnetic due to the presence of unpaired electrons. However, the magnetic properties of actinoids are higher than lanthanoids.

#### Uses

- Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.
- Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry and also in medicines.
- Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

Class XII



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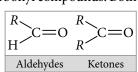
Unit 6

### Aldehydes and Ketones | Carboxylic Acids

#### **ALDEHYDES AND KETONES**

#### INTRODUCTION

Organic compounds containing carbonyl group C=O are known as carbonyl compounds. Both aldehydes and ketones come under carbonyl compounds, having general formula,  $C_nH_{2n}O$ .



#### Nomenclature

aldehydes are named according to the name of the corresponding carboxylic acid to which they are oxidised. Suffix '-ic acid' is replaced by 'aldehyde'.

Acetic acid -ic acid +aldehyde Acetaldehyde

In the common system, ketones (aliphatic or aromatic) are named by using the names of alkyl or aryl groups (in the alphabetical order) present in the molecule by adding the suffix 'ketone'.

Common System: In the common system,

**IUPAC System:** The name of aldehyde is derived by replacing the terminal '-e' of the corresponding alkane by '-al'. In ketones, the name of the individual members are derived by replacing the terminal 'e' of the corresponding alkane by 'one'. Thus, the ketones are known as alkanones.

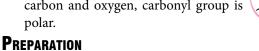
Formula	Common Name	IUPAC Name
НСНО	Formaldehyde	Methanal
CH <sub>3</sub> CHO	Acetaldehyde	Ethanal
CH <sub>3</sub> CHCHO	<i>Iso</i> -butyr-aldehyde	2-Methyl propanal
CH <sub>3</sub>		Propuna
$ \overset{3}{\text{CH}}_{2} = \overset{2}{\text{CH}} - \overset{1}{\text{CHO}} $	Acrolein	Prop-2-enal
CHO	Benzene carb-	Benzal-
	aldehyde	dehyde
CHO	Phthaldehyde	Benzene-1,2-
CHO		dicarbal- dehyde
CH₃COCH₃	Dimethyl ketone or acetone	Propanone
CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Methyl <i>n</i> -propyl ketone	Pentan-2-one
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Acetylacetone	Pentane-2, 4-dione

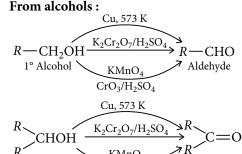
#### **ELECTRONIC STRUCTURE OF CARBONYL GROUP**

• The carbonyl carbon is  $sp^2$  hybridised thus, joined with three atoms by three sigma bonds. The fourth valence electron of carbon remains in its p-orbital and forms a  $\pi$ -bond by overlapping with p-orbital of oxygen. Since, these bonds utilise  $sp^2$ -orbitals, they lie in the same plane, having planar

another. Due to electronegativity difference of carbon and oxygen, carbonyl group is C = 0

structure and these bonds are 120° apart to one





• From carboxylic acids:

2° Alcohol

$$(RCOO)_2Ca + (HCOO)_2Ca$$

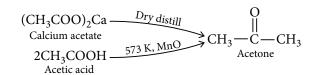
$$Calcium formate$$

$$RCOOH + HCOOH$$

$$Carboxylic Formic acid MnO, 573 K$$

CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>

Ketone



#### • From alkenes:

$$C = C \xrightarrow{H} + O_3 \xrightarrow{CHCl_3 \text{ or } CCl_4} \xrightarrow{O} C \xrightarrow{H}$$

$$Alkene \xrightarrow{H} C = O + C = O \xrightarrow{Zn/H_2O}$$

$$Aldehyde \qquad Ketone$$

#### From alkynes:

HC 
$$\equiv$$
 CH  $\xrightarrow{\text{Dil. H}_2\text{SO}_4/\text{HgSO}_4}$  CH<sub>3</sub>CHO Acetylene Acetaldehyde Acetaldehyde

CH<sub>3</sub>C  $\equiv$  CH  $\xrightarrow{\text{Propyne}}$   $\xrightarrow{\text{Dil. H}_2\text{SO}_4/\text{HgSO}_4}$  CH<sub>3</sub>  $\xrightarrow{\text{C}}$  CH<sub>3</sub>  $\xrightarrow{\text{C}}$  CH<sub>3</sub>  $\xrightarrow{\text{C}}$  CH<sub>3</sub>  $\xrightarrow{\text{C}}$  CH<sub>4</sub>  $\xrightarrow{\text{Propyne}}$   $\xrightarrow{\text{H}_2\text{O}, 333 \text{ K} \text{ (Mark. add)}}$  O Acetone

 $R - \text{C} \equiv \text{C} - \text{H} \xrightarrow{\text{(ii) } R_2\text{BH}}$   $\xrightarrow{\text{(ii) } R_2\text{O}_2/\text{OH}^-}$   $\Rightarrow$   $R - \text{CH}_2 - \text{CHO}_2$  Aldehyde

 $R - \text{C} \equiv \text{C} - R \xrightarrow{\text{(i) } B_2\text{H}_6/\text{THF}}$   $\Rightarrow$   $\Rightarrow$  R - C - CH<sub>2</sub> - R Non-terminal

Ö

Ketone

## alkynes • From gem-dihalides:

$$R - CH \xrightarrow{Cl} \xrightarrow{2KOH_{(aq)}} RCHO$$

$$1,1-Dichloroalkane \xrightarrow{-H_2O} Aldehyde$$

$$R \xrightarrow{Cl} \xrightarrow{2KOH_{(aq)}} RCHO$$

$$R \xrightarrow{-H_2O} Aldehyde$$

$$R \xrightarrow{-H_2O} R$$

$$-2KCl \xrightarrow{-H_2O} R$$

$$-2KCl \xrightarrow{-H_2O} R$$

$$-2KCl \xrightarrow{-Ketone}$$

$$R \xrightarrow{-Ketone} R$$

## NF TS

## Photoinduced annulation of 1-aryl-2-(furan/thiophen-2-yl) butane-1,3-diones

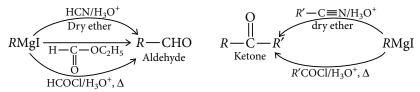
A photoinduced direct oxidative annulation of 1-aryl-2-(furan/thiophen-2-yl)butane-1,3-diones and ethyl-2-(furan-2-yl)-3-oxo-3-(aryl-2-yl)propanoates in EtOH without the need for any transition metals and oxidants provided access to highly functionalized polyheterocyclic 1-(5-hydroxynaphtho[2,1-b] furan-4-yl)ethanones and 1-(5-hydroxyfuran/thieno/pyrrolo [3,2-e]benzofuran-4-yl)ethanones. The phenomenon of

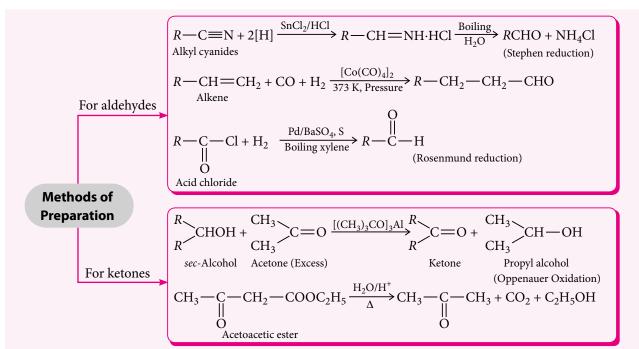
$$(Ar) \xrightarrow{O} \xrightarrow{O} \xrightarrow{R} \xrightarrow{hv (365 \text{ nm})} (Ar) \xrightarrow{OH} \xrightarrow{O} \xrightarrow{R}$$

Ar = naphthyl, phenyl, furyl, thienyl, pyrryl, benzofuryl, benzothiophene

excited-state intramolecular proton transfer (ESIPT) was observed for both 1-(5-hydroxynaphtho[2,1-b]furan-4-yl)ethanone and 1-(5-hydroxy furan/thieno/pyrrolo[3,2-e]benzofuran-4-yl)ethanone analogues.

#### • From Grignard Reagents:





#### Preparation of Aromatic Aldehydes and Ketones

#### • Commercial Method:

$$\begin{array}{c|c}
CH_3 & CHCl_2 & CH(OH)_2 & CHO \\
\hline
Oliver & 385 & M
\end{array}$$

$$\begin{array}{c|c}
Cl_2/hv & \hline
Oliver & H_2O & \hline
Oliver & H_2O & \hline
Oliver & Benzaldehyde$$

#### • Etard Reaction:

$$\begin{array}{c|c} CH_3 & CH(OCrCl_2OH)_2 & CHO \\ \hline \\ \hline \\ \hline \\ CS_2 & \hline \\ \hline \\ Toluene & Benzaldehyde \\ \end{array}$$

#### Gattermann-Koch Reaction :

#### Reimer-Tiemann Reaction

$$\begin{array}{c|c} OH & ONa & OH \\ \hline & & CHCl_3 \\ \hline & NaOH \end{array} \begin{array}{c} CHO \\ \hline & \\ & \\ & \\ \end{array} \begin{array}{c} CHO \\ \hline \\ & \\ & \\ \end{array} \begin{array}{c} CHO \\ \hline \\ & \\ \end{array} \begin{array}{c} CHO \\ \hline \\ & \\ \end{array}$$

#### • Friedel-Crafts Acylation :

$$\begin{array}{c}
COCH_{3} \\
\hline
COCH_{3} \\
\hline
COCH_{3}
\end{array}$$

$$\begin{array}{c}
COCH_{3} \\
\hline
COCH_{3}
\end{array}$$
Benzene

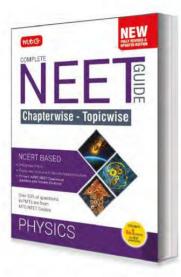
Acetophenone

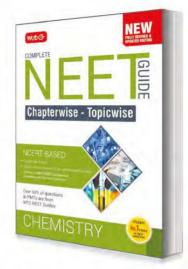
#### Fries Rearrangement :

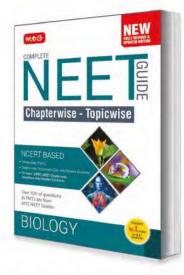
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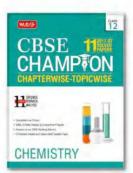




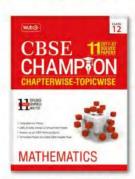
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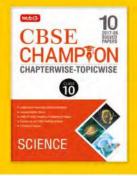






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#### PHYSICAL PROPERTIES

- Due to intermolecular dipole-dipole interactions, they have higher b.pt. than non-polar compounds and weakly polar compounds. Among isomeric aldehydes and ketones, ketones have slightly higher boiling points.
- Lower aldehydes and ketones are soluble in water due to hydrogen bonding with water. But solubility decreases as the size of hydrocarbon part increases.

#### CHEMICAL PROPERTIES

#### **Nucleophilic Addition Reactions**

In carbonyl group, due to high electronegativity of oxygen, carbon atom acquires a small positive charge and behaves as an electrophile. Therefore, the positively charged carbon is readily attacked by a nucleophile. However, during addition reaction, nucleophilic attack precedes the electrophilic attack because the anion produced is more stable than the cation.

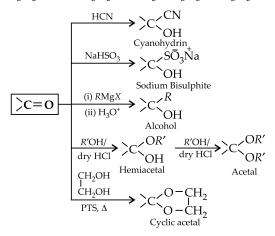
$$\begin{array}{c|c} & & & \\ &$$

• Relative reactivities of aldehydes and ketones: Aldehydes are more reactive than ketones in nucleophilic addition reactions. This is because alkyl groups are electron donating (+*I*-effect) and

thus, increase the electron density on the carbonyl carbon in ketones. Also, in ketones, the steric effect of alkyl groups decreases the reactivity. Reactivity order decreases as the steric hindrance and +I-effect of alkyl group increases.

 $\text{CH}_2\text{O} > \text{CH}_3\text{CHO} > (\text{CH}_3)_2\text{CO} > [(\text{CH}_3)_2\text{CH}]_2\text{CO}$ Due to +R effect of benzene ring, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. The decreasing order of reactivity is :

$$C_6H_5CHO > C_6H_5COCH_3 > C_6H_5COC_6H_5$$



#### **Nucleophilic Addition - Elimination Reactions**

$$(i) NH_3 \rightarrow C = NH$$

$$(ii) A \rightarrow Imine$$

$$(ii) NH_2 - Z \rightarrow C = N - Z$$

$$(iii) \Delta \rightarrow C = N - Z$$

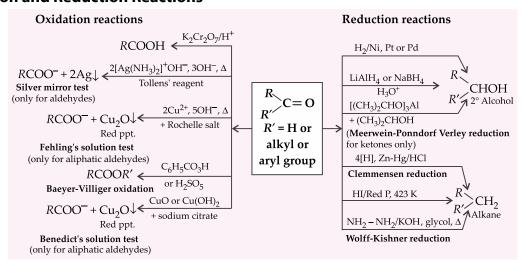
$$Derivative$$

$$(iii) \Delta \rightarrow C = N - Z$$

$$Derivative$$

$$NO_2 \rightarrow NO_2 \rightarrow NHCONH_2 \text{ etc.}$$

#### **Oxidation and Reduction Reactions**



#### **Miscellaneous Reactions**

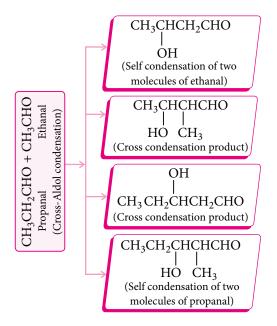
• **Aldol condensation :** Aldehydes and ketones containing at least one  $\alpha$ -hydrogen atom undergo self condensation in presence of dilute alkali to form aldol or ketol respectively.

$$2CH_{3} - C - H \xrightarrow{Dil. NaOH} CH_{3} - C - C - C - C = O \xrightarrow{H^{+}/Heat} CH_{3} - CH = CH - CHO$$

$$O \qquad H \qquad H \qquad H \qquad (Aldol)$$

$$3-hydroxybutanal$$

$$2CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{Ba(OH)_{2}} CH_{3} \xrightarrow{C} CH_{2} \xrightarrow{C} CH_{2} \xrightarrow{H^{+}/Heat} CH_{3} \xrightarrow{H^{+}/Heat} CH_{3} \xrightarrow{C} CH_{2} \xrightarrow{C} CH_{2} \xrightarrow{C} CH_{3} CH_{3} \xrightarrow{C} CH_{3} CH_{3} \xrightarrow{C} CH_{3} CH$$



• Cannizzaro reaction : Aldehydes which do not contain an α-hydrogen atom undergo disproportionation when treated with concentrated alkali solution.

$$C_6H_5CHO + C_6H_5CHO \xrightarrow{Conc. NaOH} C_6H_5CH_2OH$$
Benzaldehyde Benzyl alcohol

+ C<sub>6</sub>H<sub>5</sub>COONa Sodium benzoate

Cross Cannizzaro reaction :

$$CH_3O \xrightarrow{\hspace{1cm}} CHO + HCHO \xrightarrow{\hspace{1cm}} CH_2OH + HCOONa$$

$$\begin{array}{c} CH_3O \xrightarrow{\hspace{1cm}} CH_2OH + HCOONa \\ \\ P\text{-Methoxy-} \\ \text{benzyl alcohol} \end{array}$$

**Mechanism of Aldol Condensation** 

• Intramolecular Cannizzaro reaction :

$$\begin{array}{c|ccccc} O & O & OH & O\\ \parallel & \parallel & \parallel & \parallel\\ H-C-C-H+NaOH \longrightarrow H-CH-C-ONa\\ Glyoxal & (50\%) & OH & O\\ & & \parallel & \parallel\\ H_2C-COH & \longleftarrow\\ Glycollic acid & OH & O\\ & & \square & \square\\ \end{array}$$

Tischenko reaction :

$$2\text{CH}_{3}\text{CHO} \xrightarrow{\text{Al(OC}_{2}\text{H}_{5})_{3}} [\text{CH}_{3}\text{COOH} + \text{C}_{2}\text{H}_{5}\text{OH}]$$

$$\xrightarrow{-\text{H}_{2}\text{O}} \text{CH}_{3}\text{COOC}_{2}\text{H}_{5}$$
Ethylacetate (Ester)

Polymerisation reactions:

Polymerisation reactions:

$$\begin{array}{c}
\text{CH}_2\\
\text{O}\\
\text{O}\\
\text{CH}_2\\
\text{O}\\
\text{CH}_2\\
\text{O}\\
\text{CH}_2\\
\text{O}\\
\text{O}\\
\text{CH}_2\\
\text{O}\\
\text{O}\\
\text{O}\\
\text{O}\\
\text{CH}_2\\
\text{O}\\
\text{O}\\
\text{O}\\
\text{O}\\
\text{CH}_2\\
\text{O}\\
\text{O}\\
\text{O}\\
\text{O}\\
\text{CH}_3\\
\text{CH}\\
\text{CH}_3\\
\text{CH}_3\\
\text{CH}\\
\text{CH}_3\\
\text{CH}\\
\text{CH}_3\\
\text{Metaldehyde}$$

#### **Substitution Reactions of Aromatic Aldehydes and Ketones**

Aldehydicand ketonic groups are electron with drawing, therefore, they are deactivating and *m*-directing.

#### Distinction tests for aldehydes and ketones

Test	Aldehydes	Ketones
With Tollens' reagent	Form silver mirror	No reaction
2. With Fehling's solution	Give red precipitate (Aliphatic aldehyde)	No reaction
3. With Schiff's reagent	Give pink colour	No reaction
4. Reduction with LiAlH $_4$	Primary alcohols are formed	Secondary alcohols are formed.
5. Action with alcohol in the presence of dry HCl.	Form acetals easily	Do not form ketals easily.

#### USES

- 40% solution of formaldehyde in water is called formalin. It is used for preserving biological specimens.
- Acetaldehyde is used in the manufacturing of a number of organic compounds such as acetic acid, ethyl acetate, etc.
- Benzaldehyde is used as a starting material for the synthesis of organic compounds such as cinnamic acid, benzoyl chloride, etc.
- Acetone is extensively used as a solvent in industries and laboratories.
- Acetone is used in the preparation of chloroform, acetic anhydride. It is also one of the constituents of liquid nail polish.

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#### **CARBOXYLIC ACIDS**

#### INTRODUCTION

Organic compounds containing
—COOH as a functional group
are called carboxylic acids.

A large number of carboxylic
acids are found naturally. Some
higher members of aliphatic carboxylic acids
(C<sub>12</sub>-C<sub>18</sub>) are known as fatty acids because these are
obtained by the hydrolysis of oils and fats.

#### Nomenclature

- The common names of carboxylic acids are based on their source of origin.
- In IUPAC system, the name of the acids is derived from the corresponding alkane by replacing the terminal 'e' by suffix '-oic acid'.

,		TUDAG
Monocarboxylic acid	Common	IUPAC
	Name	Name
НСООН	Formic	Methanoic
	acid	acid
CH <sub>3</sub> COOH	Acetic acid	Ethanoic
		acid
<sup>3</sup> CH <sub>3</sub> CHCOOH	<i>Iso</i> -butyric	2-Methyl
CH <sub>3</sub> CHCOOH	acid	propanoic
CH <sub>3</sub>	(α-Methyl	acid
	propionic	
	acid)	
5 4 3 2 1	Valeric	Pentanoic
<sup>5</sup> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	acid	acid
3 2 1	α-Hydroxy-	2-Hydroxy-
$^{3}_{\text{CH}_{3}}$ $-^{2}_{\alpha}$ $^{1}_{\text{COOH}}$	propionic	propanoic
ÓН	acid or	acid
	Lactic acid	
$^{3}_{\text{CH}_{2}} = ^{2}_{\text{CHCOOH}}$	Acrylic	Prop-2-
CH <sub>2</sub> —CHCOOH	acid	enoic acid
COOH	Benzoic	Benzene-
	acid	carboxylic
		acid or
		benzoic acid
ÒН	Salicylic	2-Hy-
2 COOH	acid	droxyben-
		zoic acid

#### **ELECTRONIC STRUCTURE OF CARBOXYL GROUP**

- In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°.
- The carboxyl carbon is less electrophilic than carbonyl carbon because of the possible resonance structures.

$$-C \underset{\bigcirc \bigcirc :}{\overset{\bigcirc \square - H}{\bigcirc}} \longleftrightarrow - \underset{-}{\overset{\square - H}{\bigcirc}} \underset{\bigcirc :}{\overset{\bigcirc \square - H}{\bigcirc}} \longleftrightarrow - C \underset{\bigcirc :}{\overset{\bigcirc \square - H}{\bigcirc}}$$

#### **PREPARATION**

- $RMgX \xrightarrow{\text{(i) CO}_2/\text{dry ether}} RCOOH$ (Carbonation of Grignard reagent)
- $RCH_2OH \xrightarrow{K_2Cr_2O_7/H^+} RCOOH$ (Oxidation of 1° alcohol)
- $RCOCl \xrightarrow{H_2O} RCOOH$  (Hydrolysis of acid chlorides)
- $RCONH_2 \xrightarrow{H_2O/H^+ \text{ or } OH^-} RCOOH + NH_3$  (Hydrolysis of acidamides)

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + N_2 + H_2O$$

- $R C \equiv N \xrightarrow{\frac{2H_2O/HCl (dil.)}{\Delta}} RCOOH + NH_4Cl$ (Hydrolysis of alkyl cyanides)
- $H_2C = CH_2 + CO + H_2O \xrightarrow{H_3PO_4 \atop 623 \text{ K,}} \text{under pressure}$

H<sub>3</sub>CCH<sub>2</sub>COOH

(Koch reaction)

• 
$$CH_3 - C - R \xrightarrow{NaOI} CHI_3 + RCOONa$$
(Haloform reaction)

 $CH_3CHOH - R \xrightarrow{NaOI} CHI_3 + RCOONa$ 

COOH (Thermal decomposition of α-dioic acids)

$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$
Malonic acid

R— $CCl_3 + 4KOH$   $\longrightarrow$   $RCOOK + 3KCl + H_2O$  (Hydrolysis of 1,1,1-trihalogen derivative of alkane)

 Aromatic acids are obtained by the oxidation of alkyl benzenes.

$$CH_{2}CH_{3}$$

$$+ [O] \xrightarrow{(i) \text{ KMnO}_{4}/\text{OH}^{-}} + CO_{2} + H_{2}O$$

$$\xrightarrow{\text{Benzoic acid}} + CO_{2} + H_{2}O$$

$$\xrightarrow{\text{COOH}} + H_{3}C$$

$$COOH$$

$$\text{COOH}$$

$$\text{Terephthalic acid}$$

#### PHYSICAL PROPERTIES

- Smell: C<sub>1</sub> C<sub>3</sub> aliphatic acids have pungent smell.
   C<sub>4</sub> C<sub>9</sub> have unpleasant smell. Butyric acid has a smell of rancid butter. Higher aliphatic and aromatic acids have no smell.
- **State**: C<sub>1</sub> C<sub>9</sub> are colourless liquids. The higher acids are colourless waxy solids. Most of the aromatic acids exist as colourless crystalline solids.
- Miscibility: C<sub>1</sub> C<sub>4</sub> are freely miscible with water due to intermolecular hydrogen bonding. Solubility of higher members decreases due to increased hydrophobic interactions of the hydrocarbon part.
- Boiling points: Monocarboxylic acids have higher boiling points as compared to aldehydes, ketones and even alcohols of comparable molecular masses due to the presence of greater intermolecular hydrogen bonding.
- Melting points: Acids containing even number of carbon atoms have higher melting points as compared to their next lower and higher homologues which contain odd number of carbon atoms.

#### **ACIDIC STRENGTH**

Carboxylic acids ionise to give proton in aqueous solution.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

 $K_a$  is dissociation constant of the acid which varies with temperature.

• The acid strength is also measured in terms of  $pK_a$  values (negative logarithm of  $K_a$ ).

$$pK_a = -\log K_a$$

*i.e.*, more the value of  $pK_a$ , less acidic is the carboxylic acid indicating the lower value of  $K_a$  and smaller the value of  $pK_a$ , more acidic is the carboxylic acid indicating the higher value of  $K_a$ .

 The acidic nature can also be explained on the basis of resonating structures of carboxylate ion.

$$R \xrightarrow{\overset{\circ}{\bigcirc}} \stackrel{\circ}{\square} \xrightarrow{\overset{\circ}{\bigcirc}} -H \longleftrightarrow R \xrightarrow{\overset{\circ}{\bigcirc}} \stackrel{\circ}{\square} \xrightarrow{\overset{\circ}{\bigcirc}} H$$

 By resonating structure (B), it is clear that proton is removed to give carboxylate ion as there is positive charged oxygen atom of O—H group.

#### **EFFECT OF SUBSTITUENTS ON ACIDITY**

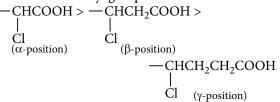
- If electron withdrawing group is present then there will be dispersal of negative charge of the carboxylate ion as a result it will be more stable than the acid not having electron withdrawing groups.
- Acidity decreases as the number of electron withdrawing group decreases.

$$i.e.$$
,  $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$ 

 The acidic strength mainly depends upon inductive effect. If +I-effect of alkyl group increases, acidity decreases.

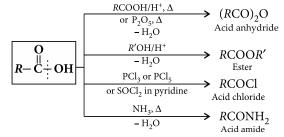
$$\begin{split} \text{HCOOH} > \text{CH}_3\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} \\ > (\text{CH}_3)_3\text{CCOOH} \end{split}$$

- If -I-effect of halogen decreases, acidity decreases.
   FCH<sub>2</sub>COOH > ClCH<sub>2</sub>COOH > BrCH<sub>2</sub>COOH > ICH<sub>2</sub>COOH
- Acidity decreases as the distance of the halogen atom from carboxyl group increases.

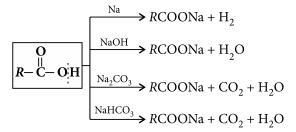


#### CHEMICAL REACTIONS

Reactions involving —OH group :



• Reactions involving proton of —OH group:

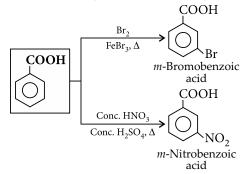


• Reaction involving —COOH group :

Reaction involving —R group :

$$\begin{array}{c|c} \mathbf{C} & \mathbf{C} \\ \mathbf{RCH_2-C-OH} & \xrightarrow{\text{(i) } X_2/\text{Red P}} R-\text{CH-COOH} \\ \hline & \text{(ii) } H_2\text{O} & \\ & X \\ \hline & \alpha\text{-Halocarboxylic acid} \\ & \text{(Hell-Volhard Zelinsky reaction)} \end{array}$$

 Ring substitution in aromatic acids: —COOH group is deactivating and meta-directing.



#### DISTINCTION BETWEEN ALCOHOLS, PHENOLS AND CARBOXYLIC ACIDS

Test	Alcohols	Phenols	Carboxylic acids
1. Action on litmus	No reaction	Turn blue litmus red	Turn blue litmus red
2. Reaction with sodium bicarbonate (NaHCO <sub>3</sub> )	No reaction	No reaction	Give effervescence due to the evolution of CO <sub>2</sub>
3. Reaction with sodium	No reaction	Form salts	Form salts
hydroxide (NaOH)	1 to reaction	T offin suits	Tom suits
4. Reaction with FeCl <sub>3</sub>	No reaction	Give characteristic colours violet, blue, red, etc.	Carboxylic acids give coloured precipitates <i>e.g.</i> , CH <sub>3</sub> COOH gives buff coloured ppt.

#### USES

- Methanoic acid is used in leather tanning and as a coagulating agent for rubber latex in rubber industry.
- Methanoic acid is used as a medicine for gout and neuritis.
- Ethanoic acid is used in the manufacture of rayon, plastics, rubber and in silk industries.
- Ethanoic acid is used as vinegar in food industry.
- Esters of benzoic acids are used in perfumery.



## Palladium-catalyzed diastereoselective synthesis of 3-arylbutanoic acid derivatives

The first palladium-catalyzed diastereoselective conjugate addition of arylboronic acids to chiral imides is reported. The catalytic system employing 4-tert-butyloxazolidin-

2-one as the chiral auxiliary in a mixed solvent system of MeOH/ $\rm H_2O$  (1:3) under an air atmosphere provides the optically active 3-arylbutanoic acid derivatives in excellent yields with high diastereoselectivity.

## **SPEED** PRACTICE

- 1. The reaction of a Grignard reagent with a carboxylic acid does not give a secondary alcohol. This is because
  - (a) Grignard reagents only react with aldehydes, ketones, esters and epoxides
  - (b) the carboxylic acid is too sterically hindered to react
  - (c) the carboxylic acid is not electrophilic enough to react
  - (d) Grignard reagent is a base, so an acid-base reaction occurs.
- **2.** Identify *A* in the given reaction,

$$\begin{array}{c} \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{CH}_3\text{MgBr}} A \\ \parallel \\ \text{O} \\ \text{CH}_3 \\ \text{(a)} \quad \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{Cl} \\ \parallel \\ \text{OH} \\ \text{(b)} \quad \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \parallel \\ \text{O} \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array}$$

3. Consider the reactions,

$$C_{2}H_{6}O \xrightarrow{Cu} A \xrightarrow{[Ag(NH_{3})_{2}]^{+}} Silver mirror observed \\ -OH, \Delta \to Y$$

$$NH_{2}NHCONH_{2} \to Z$$

Identify *A*, *X*, *Y* and *Z*.

- (a) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide
- (b) *A*-Ethanal, *X*-Ethanol, *Y*-But-2-enal, *Z*-Semicarbazone
- (c) *A*-Ethanol, *X*-Acetaldehyde, *Y*-Butanone, *Z*-Hydrazone
- (d) *A*-Methoxymethane, *X*-Ethanoic acid, *Y*-Acetate ion, *Z*-Hydrazine (**NEET 2017**)
- **4.** Structure of C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>, which on aqueous alkali hydrolysis gives a product which does not give positive iodoform test, but gives silver mirror test, is

5. In the given reaction,  $\xrightarrow{R}$   $\xrightarrow{O}$   $\xrightarrow{OH}$   $\xrightarrow{A}$ 

 $CH_3$ 

The product (*A*) is

(a) 
$$O$$
  $CH_3$  (b)  $O$   $CH_3$  (c)  $O$   $CH_3$   $O$   $CH_3$ 

6. Enolisation is maximum in case of

7. Consider the following reaction sequence,

$$\frac{\text{KMnO}_4 \text{ (dil.)}}{\text{OH}^-} \Rightarrow \frac{\text{NaIO}_4}{\text{H}_3\text{O}^+} X$$

The correct statement regarding *X* is that

- (a) it has an aldehyde functional group
- (b) it has both aldehyde and ketone functional groups
- (c) it has a ketone functional group
- (d) it has a ketone and an acid functional group.

8. The correct sequence of reagents for the following conversion will be

$$\begin{array}{ccccc}
O & & HO & CH_3 \\
& & & & & \\
CHO & & & CH_3
\end{array}$$

- (a)  $CH_3MgBr$ ,  $[Ag(NH_3)_2]^+OH^-$ ,  $H^+/CH_3OH$
- (b)  $[Ag(NH_3)_2]^+OH^-$ ,  $CH_3MgBr$ ,  $H^+/CH_3OH$
- (c) [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>OH<sup>-</sup>, H<sup>+</sup>/CH<sub>3</sub>OH, CH<sub>3</sub>MgBr
- (d)  $CH_3MgBr$ ,  $H^+/CH_3OH$ ,  $[Ag(NH_3)_2]^+OH^-$

(JEE Main 2017)

- 9. The IUPAC name of  $CH_3$ —C— $CH_2$ — $CH_2$ —CHO
  - (a) 2-oxopentanal
- (b) 4-oxopentanal
- (c) 4-formylbutan-2-one
- (d) 5-formylbutan-2-one.
- 10. In the given sequence of reactions,

$$A(C_4H_8O) \xrightarrow{Al-t-butoxide} B(ester) \xrightarrow{H_3O^+} B(Aldehyde)$$

$$H_3C$$
 $CHCOOH +$ 
 $CHCH_2OH$ 
 $H_3C$ 

A and B are

- (c) both (a) and (b)
- (d) none of the above is correct.
- 11. The correct statement(s) about the following reactions sequence is(are)

Cumene(C<sub>9</sub>H<sub>12</sub>) 
$$\xrightarrow{\text{(i) O}_2} P \xrightarrow{\text{CHCl}_3/} Q + R$$

$$Q \xrightarrow{\text{(i) NaOH}} S$$

$$Q \xrightarrow{\text{(ii) PhCH}_2\text{Br}} S$$

- (a) R is steam volatile
- (b) Q gives dark violet colouration with 1% aqueous FeCl<sub>3</sub> solution
- (c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
- (d) S gives dark violet colouration with 1% aqueous FeCl<sub>3</sub> solution. [JEE Advanced 2017]

12. Among the following four hydrogens which one is most acidic?

- (a) (i)
- (b) (ii)
- (c) (iii)
- **13.** The compounds *A*, *B* and *C* in the reaction sequence,

$$H_3C$$
 $C = O \xrightarrow{I_2} A \xrightarrow{\text{Alkali}} A \xrightarrow{\text{Ag}} B \xrightarrow{\text{dil. } H_2SO_4} C \text{ are}$ 

- (a) iodoform, ethylene, ethyl alcohol
- (b) iodoform, acetylene, acetaldehyde
- (c) iodoform, propyne, acetone
- (d) iodoform, 2-propanol, propanone.
- 14. The correct statement about the following reaction sequence is

- (a) 'R' gives an aldol condensation reaction on heating with NaOH solution
- (b) step '4' is an aromatic nucleophilic substitution reaction
- (c) the compound 'Q' gives a yellow precipitate in acetone
- (d) the end product is a mixture of three compounds.
- 15. The correct order of strength of following carboxylic acids is

**16.** Identify the product(s).

CHO | + NaOH 
$$\xrightarrow{\Delta}$$
 product(s) COOH

- **COONa**
- COONa
- CHO COONa
- (d) both (a) and (b)

17. In the following reaction,

$$H_3C$$
 CHO +  $H_2C$  CH<sub>3</sub>  $NaOMe/\Delta$ 

the product formed is

**18.** Choose the correct alternate for the given reaction sequence :

CH<sub>3</sub>CH<sub>2</sub>COOH 
$$\xrightarrow{\text{HN}_3 + \text{conc. H}_2\text{SO}_4} A$$
 (by reaction  $R_1$ )
$$A \xrightarrow{R_1} B \xrightarrow{R_2} R_2$$

- (b) CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub> HVZ CH<sub>3</sub>CH<sub>2</sub>COBr Schmidt
- $\hbox{ (c) } CH_3CH_2NH_2 \qquad HVZ \qquad CH_3CH_2COBr \quad Schmidt \\$
- (d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> Schmidt CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> HVZ
- **19.** What would be the major product in the following reaction?

- 20. Bouveault-Blanc reduction reaction involves
  - (a) reduction of an acyl halide with H<sub>2</sub>/Pd
  - (b) reduction of an anhydride with LiAlH<sub>4</sub>
  - (c) reduction of an ester with Na/C<sub>2</sub>H<sub>5</sub>OH
  - (d) reduction of a carbonyl compound with Na/Hg and HCl. (JEE Main Online 2016)
- 21. Correct statement for the given reaction is

$$\bigcirc O \xrightarrow{\text{HS}(CH_2)_2\text{HS}} \xrightarrow{\text{Raney Ni}} X + Y + \text{NiS} \downarrow$$

(a) X and Y are structural isomers

- (b) both *X* and *Y* gives only one monochlorinated product
- (c) X on oxidative ozonolysis gives gluteric acid
- (d) X and Y on reaction with  $H_2N$ -OH give oximes.
- **22.** Acids with their  $pK_a$  values are given below,

Which group has maximum electron withdrawing tendency?

- (a)  $-NO_2$  (b) -H (c) -CN (d) -OH
- 23. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha carbon, is
  - (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
  - (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
  - a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
  - (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

#### (NEET Phase-I 2016)

**24.** Consider the following aldol condensation reaction,  $CH_3-CHO\xrightarrow{H_2SO_4} CH_3-CH=CH-CHO$  the nucleophile is

(a) 
$$CH_2 = CH - OH$$
 (b)  $CH_2 = CH - \bar{O}$   $\bar{O} - H$  (c)  $\bar{C}H_2 - CHO$  (d)  $CH_3 - C - H$ 

**25.** What is the final product (*B*) of the given reaction sequence?

$$CH_{3}$$

$$ER_{2}$$

$$U.V. light$$

$$A \xrightarrow{\text{(i) KCN}} B$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

(b) 
$$CO_2H$$
  $CO_2H$   $CH_2CO_2H$   $CO_2H$   $CO_2H$   $CO_2H$   $CO_2H$ 

26. In the given Cannizzaro reaction,

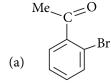
 $2\text{PhCHO} \xrightarrow{\text{OH}^{-}} \text{PhCH}_2\text{OH} + \text{PhCOO}^{-}$ the slowest step is

- (a) the attack of OH<sup>-</sup> at the carbonyl group
- (b) the transfer of hydride to the carbonyl group
- (c) the abstraction of proton from carboxylic acid
- (d) the deprotonation of PhCH<sub>2</sub>OH.
- 27. In the following species, the one which is likely to be the intermediate during benzoin condensation of benzaldehyde, is
  - (a)  $Ph-C \equiv \overset{\dagger}{O}$

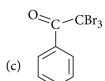
(JEE Advanced 2015)

- 28. Acetone molecules on condensation can not give
  - (a) mesityl oxide
- (b) phorone
- (c) crotonaldehyde
- (d) mesitylene.
- 29. The suitable reagent for the following conversion is

- (a) LiAlH<sub>4</sub>
- (b)  $CH_2 = O/OH^-$
- (c) Na/C<sub>2</sub>H<sub>5</sub>OH
- (d) H<sub>2</sub>/Ni
- 30. Bromination of PhCOMe in acidic medium produces mainly







$$O \gtrsim_{C} - CH_2Br$$

- 1. (d)

$$\begin{array}{c|c} CH_3 \\ H_3C - C - CH_2CH_2CH_2 \end{array} CI \xrightarrow{Rearrangement} \begin{array}{c} CH_3 \\ CH_3 \end{array}$$

- 3. (b)
- 4. (d):  $C_6H_5CH_2CHCl_2 \xrightarrow{NaOH_{(aq.)}}$

Final product will give positive silver mirror test but not iodoform test.

5. (b):

$$CH_3$$
 $CH_3$ 
 $CH_$ 

- 6. (b)
- $KMnO_4$  (dil.) OH- $\overset{\checkmark}{\text{HO}}\overset{=}{\overset{=}{\text{CH}_3}}$ OH (X)

8. (c): 
$$\frac{[Ag(NH_3)_2]^+OH^-}{Tollens' reagent} \xrightarrow{H^+/CH_3OH} \xrightarrow{Esterification}$$

$$CHO COOH$$

$$(i) 3 moles CH_3MgBr H_3C-C-CH_3$$

- 9. (b)
- 10. (a)

CH<sub>3</sub>
CH-CH<sub>3</sub>
H<sub>3</sub>C
CH<sub>3</sub>
CH-CH<sub>3</sub>

$$O_2$$
 $O_2$ 
 $O_3$ 
 $O_3$ 
 $O_4$ 
 $O_4$ 
 $O_4$ 
 $O_4$ 
 $O_4$ 
 $O_5$ 
 $O_7$ 
 $O_8$ 
 $O_9$ 
 $O_9$ 

'Q' is steam volatile due to intramolecular hydrogen bonding while 'R' undergoes intermolecular hydrogen bonding hence, has higher boiling point. 'Q' gives dark violet colouration with 1% aqueous FeCl<sub>3</sub> solution due to the presence of phenolic group while 'S' gives yellow precipitate with 2, 4-dinitrophenyl hydrazine due to the presence of aldehydic group (-CHO).

12. (b)

13. (b)

Cl

Cl

HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>, 
$$\Delta$$

(1)

Cl

HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>,  $\Delta$ 

(2)

NO<sub>2</sub>

NHNH<sub>2</sub>

NO<sub>2</sub>

NHNH<sub>2</sub>

NO<sub>2</sub>

NO<sub>2</sub>

NO<sub>2</sub>

(Q)

CH=N-NH

NO<sub>2</sub>

O<sub>2</sub>N

NO<sub>2</sub>

15. (b)

**16. (d)**: The given reaction is Cannizzaro reaction hence, two products are obtained.

$$\begin{array}{c} \text{CHO} \\ | \\ | \\ \text{COOH} \end{array} + \text{NaOH} \xrightarrow{\Delta} \begin{array}{c} \text{COONa} \\ | \\ | \\ \text{COONa} \end{array} + \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COONa} \end{array}$$

17. (c):

$$H_3C$$
 $CH_2$ 
 $CH_2$ 
 $CH_3C$ 
 $CH_4$ 
 $CH_2$ 
 $CH_4$ 
 $CH_5$ 
 $C$ 

**20.** (c) : Bouveault-Blanc reduction involves reduction of an ester in presence of Na/ $C_2H_5OH$ .

$$CH_3COOC_2H_5 + 2H_2 \xrightarrow{Na/C_2H_5OH} 2CH_3CH_2OH$$

21. (b):

$$H:S-CH_2$$
 $O_+$ 
 $H:S-CH_2$ 
 $O_+$ 
 $H:S-CH_2$ 
 $O_+$ 
 $H:S-CH_2$ 
 $O_+$ 
 $O_+$ 

**24.** (a): In acid catalysed aldol condensation, enol acts as a nucleophile and can attack on the carbonyl carbon of other molecule.

**30.** (d): Reaction in acidic medium proceeds upto monobromination stage. ♦♦

# EXAMINER'S



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.			
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.			
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.			
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.			
Section - V	<ul> <li>Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as:</li> <li>(a) If both assertion and reason are true and reason is the correct explanation of assertion.</li> <li>(b) If both assertion and reason are true but reason is not the correct explanation of assertion.</li> <li>(c) If assertion is true but reason is false.</li> <li>(d) If both assertion and reason are false.</li> </ul>			
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).			

#### **CHEMICAL KINETICS**

#### **SECTION - I**

#### **Only One Option Correct Type**

- For the first order decomposition reaction of  $N_2O_5$ , it is observed that
  - (i)  $N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + 1/2O_{2(g)}$ ;

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

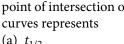
(ii)  $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$ ;

$$-\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$$

which one of the following is correct?

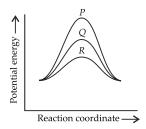
- (a) k = k'
- (b) k = 2k'
- (c) k = k'/2
- (d)  $k = k'^2$
- 2. The given figure depicts the change in concentration of species X and

Y as a function of time. The point of intersection of the two



- (a)  $t_{1/2}$
- (b)  $t_{3/4}$
- (c)  $t_{2/3}$
- (d) data insufficient to predict.

- If in a reaction,  $A \rightarrow \text{Products}$ , the concentrations of reactant A are  $C_0$ ,  $aC_0$ ,  $a^2C_0$ ,  $a^3C_0$ ... after time interval 0, t, 2t, 3t... where 'a' is constant (0 < a < 1). What is the order of reaction?
  - (a) Zero order
- (b) Second order
- (c) First order
- (d) Third order
- A first order reaction is 50% completed in  $1.26 \times 10^{14}$  s. How much time would it take for 100% completion?
  - (a)  $1.26 \times 10^{15}$  s
- (b)  $2.52 \times 10^{14}$  s
- (c)  $2.52 \times 10^{28}$  s
- (d) Infinite
- **5.** For a chemical reaction,  $k = PZe^{-E_a/RT}$ . Which of the following processes will increase the rate of reaction?
  - (a) Lowering of  $E_a$
  - (b) Lowering of P
  - (c) Lowering of Z
  - (d) Independent of all the above factors.
- If a homogeneous catalytic reaction can take place through three alternative paths as depicted in the given graph, the catalytic efficiency of paths P, Q and R would be



- (a) P > Q > R
- (b) Q > P > R
- (c) P > R > Q
- (d) R > Q > P
- 7. The activation energies of two reactions are  $E_1$  and  $E_2$  ( $E_1 > E_2$ ). If the temperature of the system is increased from  $T_1$  to  $T_2$ , the rate constant changes from  $k_1$  to  $k'_1$  in the first reaction and  $k_2$  to  $k'_2$  in the second reaction. Predict which of the following expressions is correct?

- (a)  $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$  (b)  $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$  (c)  $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$  (d)  $\frac{k_1'}{k_1} = \frac{k_2'}{k_2} = 1$
- 8. Cyclopropane rearranges to form propene as shown

$$\triangle$$
  $\longrightarrow$  CH<sub>3</sub>—CH=CH<sub>2</sub>

This follows first order kinetics. The rate constant is  $2.714 \times 10^{-3} \text{ sec}^{-1}$ . The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 s?

- (a) 0.035 M
- (b) 0.22 M
- (c) 0.145 M
- (d) 0.0018 M
- **9.** In a reaction between A and B, the initial rate of reaction  $r_0$  was measured for different initial concentrations of *A* and *B* as given below :

A/mol L <sup>-1</sup>	0.20	0.20	0.40
B/mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0/\text{mol L}^{-1}\text{s}^{-1}$	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

The order of the reaction with respect to *A* is

- (a) 1.5
- (b) 0.5
- (c) 1
- (d) 2

10. In the reaction,

$$CH_3COCH_{3(l)} \longrightarrow C_2H_{4(g)} + H_{2(g)} + CO_{(g)}$$

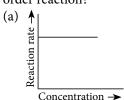
the initial pressure was 0.40 atm and after 10 min, it was found to be 0.50 atm. The rate constant for first order reaction is  $[\log 4 = 0.6021, \log 3.5 = 0.5441]$ 

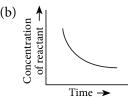
- (a)  $0.0133 \, \text{min}^{-1}$
- (b)  $0.4 \text{ s}^{-1}$
- (c)  $10 \text{ s}^{-1}$
- (d)  $0.6 \, \text{min}^{-1}$

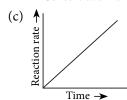
#### **SECTION - II**

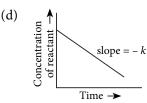
#### More than One Options Correct Type

11. Which of the following graphs is correct for a zero order reaction?









- 12. At 380 °C, the half-life period for the first order decomposition of H<sub>2</sub>O<sub>2</sub> is 360 minute. The energy of activation of the reaction is 200 kJ mol<sup>-1</sup>. What will be the time required for 75% decomposition at 450 °C?
  - (a) 20.39 min
- (b) 30.03 min
- (c) 1223.4 s
- (d) 2000 s
- 13. Which of the following statements are correct?
  - Increase in concentration of reactant increases the rate of a zero order reaction.
  - (b) Rate constant, k is equal to collision frequency 'A' if  $E_a = 0$ .
  - (c)  $\log_e k$  vs T is a straight line.
  - (d)  $\log_e k$  vs  $\frac{1}{T}$  is a straight line.

#### **SECTION - III**

#### Paragraph Type

#### Paragraph for Questions 14 and 15

A secondary alkyl halide (A) hydrolyes with alkali (B) in aqueous medium simultaneously via  $S_N1$  and  $S_N2$ pathways with rate constants  $k_1$  and  $k_2$ , respectively.

From kinetic data, it was found that a plot of  $\frac{-1}{[A]} \frac{d[A]}{dt}$ 

vs [B] is straight line with slope equal to  $2.7 \times 10^{-4}$  L mol<sup>-1</sup> min<sup>-1</sup> and intercept equal to 1.02×10<sup>-3</sup>Lmol<sup>-1</sup>min<sup>-1</sup>. Minimum initial concentration of [A] = 0.2 M and [B] i.e.,  $[OH^{-}] = 0.5 \text{ M}$ .

- 14. The value of overall rate constant for the hydrolysis of A (in L mol<sup>-1</sup> min<sup>-1</sup>) is
  - (a)  $2.7 \times 10^{-4}$
- (b)  $1.02 \times 10^{-3}$
- (c)  $1.29 \times 10^{-3}$
- (d) none of these.

- 15. The initial rate of consumption of secondary alkyl halide (in M min<sup>-1</sup>) is
  - (a)  $0.36 \times 10^{-3}$
- (b)  $2.89 \times 10^{-5}$
- (c)  $2.31 \times 10^{-4}$
- (d)  $2.31 \times 10^{-3}$

#### Paragraph for Questions 16 and 17

Temperature has a significant effect on the rate of reaction. Quantitatively, the effect of temperature is explained by Arrhenius equation,  $k = Ae^{-E_a/RT}$  in which,  $E_a$  represents the activation energy of the reaction. Collision theory explains how the rate of reaction depends upon the energy factor and orientation factor i.e., for any collision to be effective, the energy of the colliding molecules should be greater than threshold value and should have proper orientation at the time of collision. Mathematically, collision theory follows,  $k = PZ_{AB} e^{-E_a/RT}$ .

- **16.** The temperature coefficient for most of the reactions lies between
  - (a) 1 and 3
- (b) 2 and 3
- (c) 1 and 4
- (d) 2 and 4
- 17. When  $\log k$  is plotted against 1/T, where k is rate constant and T is temperature, a straight line is obtained with a slope of -7000 K. The energy of activation of the reaction is nearly
  - (a) 114 kJ mol<sup>-1</sup>
- (b) 124 kJ mol<sup>-1</sup>
- (c) 134 kJ mol<sup>-1</sup>
- (d) 144 kJ mol<sup>-1</sup>

#### **SECTION - IV**

#### Matching List Type

18. Match the List-I with List-II and select the correct answer using the codes given below the Lists:

#### List I

#### List II

- A.  $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+}$  $C_6H_{12}O_6 + C_6H_{12}O_6$
- p. Pseudo first order
- B.  $CH_3COOC_2H_5 \xrightarrow{HOH} \overrightarrow{H^+ \text{ or } OH^-}$
- q. Zero order

 $CH_3COOH + C_2H_5OH$ 

- C.  $H_2 + Cl_2 \xrightarrow{hv} 2HCl$
- r. Second order
- D.  $CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$  s. First order
  - C D
- (a) p r, p
- (b) p p, r r q
- (c) p r S q
- (d) r, s

19. Match the List-I with List-II and select the correct answer using the codes given below the Lists:

#### List I

- A. Mathematical expression p. Rate constant for rate of reaction
- Rate of reaction for zero q. Rate law order reaction is equal to
- C. Units of rate constant r. Slowest step for zero order reaction is same as that of
- D. Order of a complex s. Rate of reaction is determined by reaction
  - C D
- (a) q
- (b) p
- (c) p
- (d) r

#### **Assertion Reason Type**

**20. Assertion**: A catalyst does not alter the heat of reaction.

**Reason**: Catalyst increases the rate of reaction.

21. Assertion: For molecules to interact, they must approach each other so closely to collide with each other.

**Reason:** Rearrangement of chemical bonds occurs during collision.

22. Assertion: The order of a reaction can have a fractional value.

**Reason**: The order of reaction cannot be written from the balanced chemical equation.

#### **SECTION - VI**

#### Integer Value Correct Type

- **23.** A reactant (*A*) forms two products,
  - $A \xrightarrow{k_1} B$ ; Activation energy  $E_{a_1}$   $A \xrightarrow{k_2} C$ ; Activation energy  $E_{a_2}$
  - If  $E_{a_2} = 2E_{a_1}$ , then  $k_1$  and  $k_2$  are related as
  - $k_1 = x \times k_2 e^{E_{a_1}/RT}$ . Find out the value of 'x'.
- **24.** The  $t_{1/2}$  for the decomposition of CH<sub>3</sub>CHO at constant temperature and at initial pressure of 340 mm of Hg and 170 mm of Hg were 410 s and 820 s respectively. Calculate the order of the reaction.
- **25.** For the reaction,  $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$ , the initial concentration of  $I^-$  was 0.20 mol  $L^{-1}$  and the concentration after 20 min was 0.18 mol L<sup>-1</sup>. Then, the rate of formation of  $I_2$  in mol  $L^{-1}$  min<sup>-1</sup> is written as  $y \times 10^{-4}$ . The value of 'y' is

#### AMINES AND BIOMOLECULES

#### **SECTION - I**

#### Only One Option Correct Type

- 1. The most reactive amine towards dilute hydrochloric
  - (a) CH<sub>3</sub>NH<sub>2</sub>
- (b)  $H_3C$  NH
- (c)  $H_3C$  NH-CH<sub>3</sub>
- 2. Two aldopentoses 'X' and 'Y' give the same osazone derivative. 'X' is oxidised to an optically active aldaric acid by dilute nitric acid. Ruff degradation of 'Y' gave a tetrose which was similarly oxidised to an optically active aldaric acid.

Assign the structures of X' and Y' from the following.

- CHO **CHO** -OH -OH H OH-H — ОН —ОН CH<sub>2</sub>OH ĊH<sub>2</sub>OH II CHO CHO **—**Н HO-—н HO-—он -н H-НО L\_OH —н HO-ĊH<sub>2</sub>OH CH<sub>2</sub>OH
- (a) X = I, Y = IV
- (b) X = IV, Y = I
- (c) X = III, Y = II
- (d) X = II, Y = III
- 3. A compound of molecular formula C<sub>3</sub>H<sub>9</sub>N when reacts with benzene sulphonyl chloride gives a product soluble in dilute NaOH solution. The compound should be
  - (a)  $(CH_3)_3N$
- (b)  $(CH_3)_2CHNH_2$

Ö

- (d) all of these.
- 4. Which statement is incorrect regarding peptide bond?
  - (a) C-N bond length in proteins is longer than usual bond length of C-N bond.
  - (b) Spectroscopic analysis shows planar structure of -C-NH- bond.

- (c) C-N bond length in proteins is smaller than usual bond length of C-N bond.
- (d) Both (b) and (c)
- Propionitrile reacts with 'A' followed by hydrolysis to give 'B'. The compound 'B' on addition of HCN gives 'C'. The compound 'C' on reduction gives 1-amino-2-ethyl-4-methyl-2-pentanol. Identify 'A'.

  - (a)  $(CH_3)_3CCH_2MgX$  (b)  $CH_3CH_2CH_2MgX$
  - (c)  $C_2H_5MgX$
- (d)  $(CH_3)_2CHCH_2MgX$
- What will be the yields of the given reaction?

$$(a) \qquad \begin{array}{c} \text{NH}_2 \\ + \text{PhCOCl} \xrightarrow{\text{Pyridine}} ? \\ \text{COPh} \\ \text{(b)} \end{array}$$

$$(c) \qquad \begin{array}{c} \text{NH} \\ \text{COCl} \\ \text{(d)} \end{array}$$

Which of the following chemical units is certainly to be found in an enzyme?

- An electric current is passed through an aqueous solution of a mixture of alanine (isoelectric point 6.0), glutamic acid (3.2) and arginine (10.7) buffered at pH 6. What is the fate of the three acids?
  - (a) Glutamic acid migrates to anode at pH 6. Arginine is present as a cation and migrates to the cathode. Alanine is a dipolar ion uniformly distributed in solution.
  - (b) Glutamic acid migrates to cathode and others remain uniformly distributed in solution.
  - (c) All three remain uniformly distributed in solution.
  - (d) All three move to cathode.

9. When the imidazole ring of histidine is protonated, tendency of nitrogen to be protonated (proton migrates from - COOH) is in the order of

- (a)  $\beta > \gamma > \alpha$
- (b)  $\gamma > \beta > \alpha$
- (c)  $\gamma > \alpha > \beta$
- (d)  $\beta > \alpha > \gamma$
- **10.** Which of the following statements are incorrect?
  - I. Albumin is a simple protein.
  - II. Amino acid alanine contains an acidic side chain.
  - III. Insulin is a hormone.
  - IV. Muscles contain the protein keratin.
  - (a) I, II
- (b) III, IV
- (c) I, III
- (d) II, IV

#### **SECTION - II**

#### More than One Options Correct Type

- 11. Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Which of the following are acidic?
  - (a) (CH<sub>3</sub>)<sub>2</sub>CH—CH—COOH

NH<sub>2</sub>
(b) HOOC—CH<sub>2</sub>—CH<sub>2</sub>—CH—COOH

- (c) H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH
- (d) HOOC— $\mathrm{CH_2}$ — $\mathrm{CH}$ — $\mathrm{COOH}$
- 12. Under which of the following reaction conditions, aniline gives p-nitro derivative as the major product?
  - (a) Acetyl chloride/pyridine followed by conc.  $H_2SO_4 + conc. HNO_3$
  - (b) Acetic anhydride/pyridine followed by conc.  $H_2SO_4 + conc. HNO_3$
  - (c) Dil. HCl followed by conc. H<sub>2</sub>SO<sub>4</sub> + conc. HNO<sub>3</sub>
  - (d) NaNO<sub>2</sub> + HCl at 0-5  $^{\circ}$ C

13. The product of the reaction,

D-glyceraldehyde  $\xrightarrow{\text{Me}_2\text{CO}} \xrightarrow{\text{H}_2\text{C}=\text{CHMgCl}} \xrightarrow{\text{O}_3} \xrightarrow{\text{Zn/H}_2\text{O}}$ is/are?

(c) 
$$\begin{array}{c} CH_2OH \\ HO \\ \hline \\ CH_2OH \end{array}$$
 (d)  $\begin{array}{c} CHO \\ HO \\ \hline \\ CH_2OH \end{array}$  (d)  $\begin{array}{c} CHO \\ HO \\ \hline \\ CH_2OH \end{array}$ 

#### **SECTION - III**

#### Paragraph Type

#### Paragraph for Questions 14 and 15

RCONH2 is converted into RNH2 by means of Hoffmann bromamide degradation.

$$Cl \xrightarrow{O}_{NH_2} Cl \xrightarrow{O}_{NHBr}$$

$$Cl \xrightarrow{(ii)} N \xrightarrow{O}_{NHBr}$$

$$Cl \xrightarrow{(iv)} Cl \xrightarrow{(iii)} N \xrightarrow{\bar{N}} -Br$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hoffmann degradation reaction is an intramolecular reaction.

- 14. How can the conversion of (i) to (ii) be brought about?
  - (a) KBr
- (b)  $KBr + CH_3ONa$ (d)  $Br_2 + KOH$
- (c) KBr + KOH
- 15. Which is the rate determining step in Hoffmann bromamide degradation?
  - (a) Formation of (vi)
- (b) Formation of (ii)
- (c) Formation of (iii)
- (d) Formation of (iv)

#### Paragraph for Questions 16 and 17

All monosaccharides (both aldoses and ketoses) containing five or six carbon atoms can have two cyclic structures namely furanose and pyranose forms. Due to cyclic nature, the carbon atom of the aldehyde/keto group of the monosaccharide becomes chiral and consequently each monosaccharide whether in pyranose or in furanose form exists in two stereoisomeric forms called  $\alpha$ - and  $\beta$ -anomer. In case, the two stereoisomers differ in configuration at a chiral carbon other than the anomeric carbon, then they are called epimers.

- **16.**  $\alpha$ -D-(+)-glucose and  $\beta$ -D-(+)-glucose are
  - (a) enantiomers
- (b) geometrical isomers
- (c) epimers
- (d) anomers.
- 17. Glucose and galactose are
  - (a) anomers
- (b)  $C_2$ -epimers
- (c) C<sub>3</sub>-epimers
- (d)  $C_4$ -epimers.

#### **SECTION - IV**

#### **Matching List Type**

**18.** Match the reactions given in List I with the statements given in List II and select the correct answer using the codes given below the lists:

	List I		List II
P.	Ammonolysis	1.	Amine with lesser number of carbon atoms.
Q.	Gabriel phthalimide synthesis	2.	Detection test for primary amines.
R.	Hoffmann Bromamide reaction	3.	Reaction of phthalimide with KOH and <i>R—X</i> .
S.	Carbylamine reaction	4.	Reaction of alkylhalides with NH <sub>3</sub> .
P	Q	R	$\mathbf{s}$
(a) 3	4	1	2
(b) 2	4	3	1
(c) 1	3	4	2
(d) 4	3	1	2

19. Match the enzymes given in List I with their catalytic reaction given in List II and select the correct answer using the codes given below the lists:

	Lis (Er	t I nzymes	)		st II eactions)
P.	Invertase 1.			ecomposition of urea into $H_3$ and $CO_2$	
Q.	. Maltase 2.		2.		onversion of glucose into nyl alcohol
R.	Pep	osin	3.	•	vdrolysis of maltose into
S.	Ure	ease	4.	Ну	drolysis of cane sugar
T.	Zyı	mase	5.	•	vdrolysis of proteins into ptides
	P	Q	R	S	T
(a)	4	3	5	1	2
(b)	2	5	4	3	1
(c)	4	3	1	2	5
(d)	5	1	3	4	2

#### **SECTION - V**

#### **Assertion Reason Type**

- **20. Assertion** : *N*, *N*-Diethylbenzene sulphonamide is insoluble in alkali.
  - **Reason :** Sulphonyl group is attached to electronegative nitrogen atom.
- **21. Assertion**: In presence of enzyme, substrate molecule can be attacked by the reagent effectively. **Reason**: Active sites of enzymes hold the substrate molecule in a suitable position.
- 22. Assertion: In strongly acidic solutions, aniline becomes less reactive towards electrophilic reagents. Reason: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

#### SECTION - VI

#### **Integer Value Correct Type**

- 23. In *D*-talose, the total number of chiral centres is
- 24. Amongst the following, the total number of amides which undergo Hoffmann bromamide reaction are: C<sub>6</sub>H<sub>5</sub>CONH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CONHCH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>CON(CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>CONH<sub>2</sub>, CH<sub>3</sub>CONHCH<sub>3</sub>, CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CHCONHCH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>CHCONH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CHCON(CH<sub>3</sub>)<sub>2</sub>
- **25.** Amongst the following, the maximum number of water soluble vitamins are A, B<sub>1</sub>, B<sub>2</sub>, B<sub>6</sub>, H, B<sub>12</sub>, C, D, E and K.

#### **SOLUTIONS**

#### **CHEMICAL KINETICS**

1. (b): For the reaction,

$$\begin{aligned} &\mathbf{N}_2\mathbf{O}_{5(g)} \longrightarrow 2\mathbf{N}\mathbf{O}_{2(g)} + 1/2\mathbf{O}_{2(g)} \\ &\mathbf{R}ate = -\frac{d[\mathbf{N}_2\mathbf{O}_5]}{dt} = k[\mathbf{N}_2\mathbf{O}_5] \\ &\mathbf{For the reaction, } 2\mathbf{N}_2\mathbf{O}_{5(g)} \longrightarrow 4\mathbf{N}\mathbf{O}_{2(g)} + \mathbf{O}_{2(g)} \\ &\mathbf{R}ate = -\frac{1}{2}\frac{d[\mathbf{N}_2\mathbf{O}_5]}{dt} = k'[\mathbf{N}_2\mathbf{O}_5] \\ &\Rightarrow -\frac{d[\mathbf{N}_2\mathbf{O}_5]}{dt} \Rightarrow 2k'[\mathbf{N}_2\mathbf{O}_5] = k[\mathbf{N}_2\mathbf{O}_5] \end{aligned}$$

- (a) 2. 3. (c)
- (d): Reaction would be 100% complete only after infinite time which cannot be calculated.
- (a) **5.**
- (d): The catalytic efficiency of a catalyst is measured in terms of the decrease in activation energy of the reaction. A catalyst is more efficient if it decreases the activation energy to a larger extent. Thus, the correct order of catalytic efficiency is R > Q > P.

7. **(b)**: 
$$\log \frac{k_1'}{k_1} = \frac{E_1}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$
 ...(i)  
 $\log \frac{k_2'}{k_2} = \frac{E_2}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$  ...(ii)

As, 
$$E_1 > E_2$$

From (i) and (ii), we get

$$\log \frac{k_1'}{k_1} > \log \frac{k_2'}{k_2} \Rightarrow \frac{k_1'}{k_1} > \frac{k_2'}{k_2}$$

8. **(b)**: 
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

where, (a - x) is the concentration of cyclopropane left after 100 s.

$$2.714 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.29}{(a-x)}$$

$$\Rightarrow \frac{0.2714}{2.303} = \log \frac{0.29}{(a-x)} \Rightarrow 0.118 = \log \frac{0.29}{(a-x)}$$

- $\Rightarrow$  (a-x) = 0.22 M
- **9.** (a): Let rate =  $k[A]^x [B]^y$

From the given data,

$$5.07 \times 10^{-5} = k[0.20]^x [0.30]^y$$
 ...(i)  
 $5.07 \times 10^{-5} = k[0.20]^x [0.10]^y$  ...(ii)

$$5.07 \times 10^{-5} = k[0.20]^x [0.10]^y$$
 ...(ii)

$$1.43 \times 10^{-4} = k[0.40]^x [0.05]^y$$
 ...(iii)

From eq. (i) and (ii)

$$1 = \frac{[0.30]^y}{[0.10]^y} \implies y = 0$$

By dividing eq. (iii) by eq. (ii)
$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \frac{[0.10]^y}{[0.05]^y}$$

as 
$$v = 0$$

Thus, 
$$2.82 = \left(\frac{0.40}{0.20}\right)^x \implies (2)^x = 2.82 \implies x = 1.5$$

10. (a):  $CH_3COCH_{3(I)} \longrightarrow C_2H_{4(g)} + H_{2(g)} + CO_{(g)}$ Initial 0.4 atm 0 0 0 pressure

After 10 min (0.4 - x) atm x atm

Total pressure = 0.4 - x + x + x + x = 0.50 atm

$$\Rightarrow$$
 2x = 0.10 or x = 0.05 atm

$$k = \frac{2.303}{10} \log \frac{0.4}{0.4 - 0.05} = \frac{2.303}{10} \times 0.0580$$
$$= 0.01335 \text{ min}^{-1}$$

11. (a, d): For a zero order reaction,

rate = 
$$-\frac{d[A]}{dt} = k$$
 or  $\frac{d[A]}{dt} = -k$ 

On integrating we get,  $\int d[A] = -\int k \, dt$ 

$$[A] = -kt + I \qquad \dots(i)$$

When, t = 0 then  $[A] = [A]_0$ 

$$I = [A]_0$$

On putting the value of *I* in eq. (i)

$$[A] = -kt + [A]_0$$

 $\therefore$  A graph of [A] vs t is a straight line with slope = -k.

12. (a, c): 
$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{360} = 1.925 \times 10^{-3} \text{ min}^{-1}$$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \, R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log_{10} \frac{k_2}{1.925 \times 10^{-3}} = \frac{200 \times 10^3}{2.303 \times 8.314} \left[ \frac{723 - 653}{653 \times 723} \right]$$

$$t = \frac{2.303}{k_2} \log_{10} \frac{a}{a - x} \Rightarrow \frac{2.303}{0.068} \log_{10} \frac{100}{25}$$

 $\therefore$  t = 20.39 min = 1223.4 s

- 13. (b, d)
- 14. (c): Through  $S_N1$  pathway:

$$RX(A) \longrightarrow R^+ + X^- \xrightarrow{OH^-} R \longrightarrow OH$$
  
 $Rate = \frac{-d[A]}{dt} = k_1[RX]$  ...(i)

Through S<sub>N</sub>2 pathway:

$$HO^- + R - X \longrightarrow HO - R + X^-$$

Rate = 
$$\frac{-d[A]}{dt} = k_2[RX][OH^-]$$
 ...(ii)

Combining eq. (i) and (ii),

Rate = 
$$\frac{-d[A]}{dt} = k_1[RX] + k_2[RX][OH^-]$$
  
 $\frac{-d[A]}{dt} = k_1[A] + k_2[A][B]$   
 $\frac{-d[A]}{dt} = [A](k_1 + k_2[B])$  ...(iii)

$$\frac{1}{[A]} \frac{-d[A]}{dt} = k_1 + k_2[B]$$
 ...(iv)

Comparing this with equation of straight line,

Slope 
$$(m) = k_2 = 2.7 \times 10^{-4} \text{ L mol}^{-1} \text{ min}^{-1}$$
  
=  $0.27 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ 

Intercept (c) =  $k_1 = 1.02 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ Overall rate constant =  $k_1 + k_2$ =  $(0.27 + 1.02) \times 10^{-3} = 1.29 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ 

$$= (0.27 + 1.02) \times 10^{-3} = 1.29 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$$

15. (c): 
$$[RX]_0 = [A]_0 = 0.2 \text{ M}; [B]_0 = [OH^-] = 0.5 \text{ M}$$
  
From Eq. (iii),  $\frac{-d[A]}{dt} = [A](k_1 + k_2[B])$   
 $= 0.2(1.02 \times 10^{-3} + 0.27 \times 10^{-3} \times 0.5)$   
 $= 0.2 \times 10^{-3} (1.02 + 0.135)$   
 $= 0.2 \times 10^{-3} \times 1.155 = 2.31 \times 10^{-4} \text{ M min}^{-1}$ 

17. (c): Slope = 
$$-\frac{E_a}{2.303 R}$$
  
 $E_a = -2.303 \times R \times \text{slope}$   
=  $-2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (-7000 \text{ K})$   
=  $134029.9 \text{ J mol}^{-1} \approx 134 \text{ kJ mol}^{-1}$ 

- 18. (b) 19. (a) **20.** (b)
- 21. (b)
- 23. (1):  $A \xrightarrow{k_1} B$ ,  $A \xrightarrow{k_2} C$ By Arrhenius equation,  $k_1 = A' e^{-E_{a_1}/RT}$  and  $k_2 = A' e^{-E_{a_2}/RT}$ (A' is Arrhenius constant) (:

$$k_{2} = A'e^{-2E_{a_{1}}/RT}$$

$$\frac{k_{1}}{k_{2}} = \frac{A'e^{-E_{a_{1}}/RT}}{A'e^{-2E_{a_{1}}/RT}} = e^{E_{a_{1}}/RT} \implies k_{1} = k_{2}e^{E_{a_{1}}/RT}$$

On comparing this equation with the given equation, we get x = 1.

**24.** (2):  $t_{1/2} \propto [CH_3CHO]^{1-n}$ , where *n* is the order of reaction.

$$\frac{410}{820} = \left(\frac{340}{170}\right)^{1-n} \implies \log \frac{410}{820} = (1-n)\log\left(\frac{340}{170}\right)$$
$$\log(1/2) = (1-n)\log 2 \implies n = 2$$

**25.** (5): Rate of disappearance of  $I^-$ 

$$-\frac{d[I^{-}]}{dt} = \frac{(0.20 - 0.18) \text{ mol } L^{-1}}{20 \text{ min}}$$
$$= 10^{-3} \text{ mol } L^{-1} \text{ min}^{-1}$$

Rate of reaction = 
$$-\frac{1}{2} \frac{d[\Gamma]}{dt} = +\frac{d[I_2]}{dt}$$

 $\therefore$  Rate of formation of  $I_{2}$ :

$$\frac{d[I_2]}{dt} = -\frac{1}{2} \frac{d[I^-]}{dt} = \frac{10^{-3}}{2}$$

 $= 5 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$ 

Comparing it with  $y \times 10^{-4}$  then y = 5

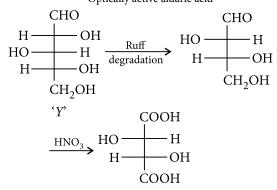
#### **AMINES AND BIOMOLECULES**

- (b): Secondary amines are most reactive towards dilute HCl because electron density on N is more than primary amines due to presence of two alkyl groups. Though tertiary amines have maximum electron density on N but they suffer steric hindrance.
- (c): 'X' and 'Y' have same osazone derivative, it means configuration at C-3 and C-4 is the same.

 $X \xrightarrow{\text{Dil. HNO}_3}$  optically active aldaric acid,



Optically active aldaric acid



Optically active aldaric acid

3. (b): 
$$H_3C$$
  $CH-NH_2+ClO_2S$   $O$ 

Primary amine Benzene sulphonyl chloride

NaNSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> NaOH H<sub>3</sub>C  $O$ 

CH(CH<sub>3</sub>)<sub>2</sub>  $O$ 

Soluble

5. (d): 
$$(CH_3)_2CHCH_2MgX + CH_3CH_2CN$$
Propionitrile

 $(CH_3)_2CHCH_2 - C = O$ 
 $(CH_3)_2CHCH_2 - C = O$ 
 $(CH_3)_2CHCH_2 - C = O$ 
 $(CH_2CH_3)$ 
 $(CH_3)_2CH - CH_2 - C = O$ 
 $(CH_2CH_3)$ 
 $(CH_3)_2CH - CH_2 - C = OH$ 
 $(CH$ 

6. (a)

7. (c): Since enzymes are proteins they contain – CO–NH– group.

1-amino-2-ethyl-4-methyl-2-pentanol

**8.** (a): At pH = 6, glutamic acid exists as a dianionic species.

$$\begin{array}{c}
- & \text{OOC} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\
\hline
\text{COO}
\end{array}$$
\tag{(+)}
\text{NH}\_3
\to \text{net charge (-1)}

So it migrates to anode while arginine exists as cationic species.

$$H_2N$$
 $(+)$ 
 $CNH_2-(CH_2)_3CH$ 
 $(+)$ 
 $COO$ 
 $(+)$ 
 $COO$ 
 $(+)$ 
 $COO$ 

So, it migrates to cathode. Alanine does not migrate to any electrode at its isoelectric point.

9. (c)

10. (d)

11. (b, d)

12. (a, b)

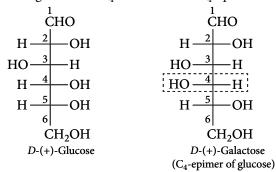
13. (a, d): 
$$H \longrightarrow OH \xrightarrow{Me_2CO} HCHO$$
 $CHO$ 
 $CHO$ 
 $CHO$ 
 $CHO$ 
 $CHO$ 
 $CHO$ 
 $CH_2OH$ 
 $CH_2OH$ 
 $CH_2CHMgCl$ 
 $CH=CH_2$ 
 $CH=CH_2$ 
 $CH=CH_2$ 
 $CH=CH_2$ 
 $CH=CH_2$ 
 $CH_2OH$ 
 $CH_2OH$ 
 $CHO$ 
 $C$ 

14. (d): Cl 
$$\stackrel{O}{\longrightarrow}$$
  $\stackrel{NH_2}{\longrightarrow}$  + Br<sub>2</sub>  $\stackrel{KOH}{\longrightarrow}$  Cl  $\stackrel{O}{\longrightarrow}$   $\stackrel{NHBr}{\longrightarrow}$  + KBr + H<sub>2</sub>O

**15.** (d): The rate determining step is probably loss of Br<sup>-</sup> to form isocyanates as this is the slowest step.

**16.** (d):  $\alpha$ -D-(+)-glucose and  $\beta$ -D-(+)-glucose are differ in configuration at  $C_1$  and hence are anomers.

**17.** (d): Glucose and galactose are differ in configuration at  $C_4$  and hence are  $C_4$ -epimers.



18. (d) 19. (a)

**20. (b)**: *N*, *N* - Diethylbenzene sulphonamide is a tertiary amine which does not have acidic H attached to N-atom. Thus, it is insoluble in alkali.

**21.** (a): In presence of enzyme, substrate molecule can be attacked by the reagent effectively because active sites of enzymes hold the substrate molecule in a suitable position.

22. (a) 23. (4)

**24.** (3): Only 1° amides, *i.e.*, C<sub>6</sub>H<sub>5</sub>CONH<sub>2</sub>, CH<sub>3</sub>CONH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CHCONH<sub>2</sub> undergo Hoffmann bromamide reaction.

**25. (6)**: Vitamins of B group, *i.e.*, B<sub>1</sub>, B<sub>2</sub>, B<sub>6</sub>, B<sub>12</sub>, H and vitamin C are water soluble.



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CHAPTERWISE PRACTICE PAPER : BIOMOLECULES | POLYMERS | CHEMISTRY IN EVERYDAY LIFE

Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carry 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.
- 1. Classify the following as addition and condensation polymers:
  - Terylene, bakelite, polyvinyl chloride, polythene
- **2.** The base sequence in a fragment of one strand of DNA is:

AAT TCC CGG

What is the base sequence of the complementary strand?

- **3.** What is the difference between Buna-N and Buna-S?
- **4.** Name the enzyme that converts sucrose into glucose and fructose. Write chemical equation also.
- **5.** Give one important use of each of the following :
  - (i) Equanil
- (ii) Morphine
- **6.** Differentiate between nucleotides of DNA and RNA.
- 7. What are natural and synthetic polymers? Give two examples of each type.
- 8. What factors are responsible for the stability of  $\alpha$ -helix structure of proteins? Why is it named as  $3.6_{13}$  helix?

- 9. Why do we require artificial sweetening agents?
  - What are fillers and what role these fillers play in soap?
- **10.** How does the presence of double bonds in rubber molecules influence their structure and reactivity?
- 11. Define the following as related to proteins:
  - (i) Peptide linkage (ii) I(iii) Fibrous proteins
    - (ii) Primary structure
- **12.** What are anionic detergents? How are they prepared? Write their two main uses.
- **13.** What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester and the reaction involved in its preparation.
- 14. Which moieties of nucleotides are involved in the formation of phosphodiester linkages present in dinucleotides? What does the word diester in the name of linkage indicate? Which acid is involved in the formation of this linkage?

**OR** 

Name the sources and the main diseases caused due to lack of vitamins A, H and E.

- **15.** Define the following with examples:
  - (i) Semi-synthetic polymers
  - (ii) Network polymers
  - (iii) Fibres
- **16.** (a) Name the type to which the following drugs belong and give their uses.
  - (i) Luminal (ii) Streptomycin
  - (iii) Analgin
  - (b) Give one more example of each class.
- **17.** What are the different types of RNA found in cells of organisms? State the functions of each type.
- **18.** Write the names and molecular structures of the monomers of the following polymers. Give one use of each specifying the property responsible for this use.
  - (i) Glyptal
- (ii) Nylon-6
- (iii) Neoprene
- **19.** Explain the role of allosteric site in enzyme inhibition.
- **20.** Phenol and formaldehyde undergo condensation to give a polymer (*A*) which on heating with formaldehyde gives a thermosetting polymer (*B*). Name the polymers. Write the reactions involved in the formation of (*B*). What is the structural difference between these two polymers?
- **21.** (i) Which one of the following is a food preservative?

  Equanil, morphine, sodium benzoate
  - (ii) Why is bithional added to soap?
  - (iii) Which class of drugs is used in sleeping pills?
- **22.** (i) What is denaturation and renaturation of proteins?
  - (ii) Amylase present in the saliva becomes inactive in the stomach. Explain.
- 23. Gopal and Gaurav both were going to play cricket match in the ground. Suddenly both of them saw an accident between a car and a motorcycle. The biker had fallen down. Both of them moved towards the biker and provided him the first aid. They put dettol over his scratches on hands and legs and gave him a painkiller.
  - (i) Why did the boys used dettol over scratches of biker?
  - (ii) What is the chemical composition of dettol?

- (iii) What is the chemical present in antiseptic soap?
- (iv) What are the values shown by Gopal and Gaurav?
- **24.** Answer the following questions:
  - (i) In E. Coli DNA, the AT/GC ratio is 0.93. If the number of moles of adenine in the DNA sample is 4,65,000, calculate the number of moles of guanine present.
  - (ii) In an aqueous solution of glucose, it is mainly an equilibrium mixture of  $\alpha$ -D-(+)-glucose with specific rotation  $[\alpha]_D = +112^\circ$  and  $\beta$ -D-(+)-glucose with specific rotation,  $[\alpha]_D = +18.7^\circ$ . The specific rotation of the equilibrium mixture is +52.7°. Find the percentage composition of the equilibrium mixture.

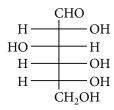
#### OR

- (a) Explain the following:
  - (i) Sucrose is dextrorotatory but the mixture obtained after hydrolysis is laevorotatory.
  - (ii) Amino acids behave like salts rather than simple amines or carboxylic acids.
- **(b)** How do enzymes help a substrate to be attacked by the reagent effectively?
- **25.** (i) Name a substance which can be used as an antiseptic as well as disinfectant.
  - (ii) Why are cimetidine and ranitidine better antacids than sodium bicarbonate or magnesium or aluminium hydroxide?
  - (iii) How do antiseptics differ from disinfectants? Give one example of each.

#### OR

Answer the following questions:

- (i) If water contains dissolved calcium bicarbonate, out of soaps and synthetic detergents which one will you use for cleaning clothes?
- (ii) Label the hydrophilic and hydrophobic parts in the following compounds. Also, give their names.
  - (a)  $CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$
  - **(b)**  $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
  - (c)  $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$
- **26.** Answer the following questions :
  - (a) On electrolysis in acidic solution, glycine migrates towards cathode while in alkaline solution, it migrates towards anode. Explain.
  - **(b)** The Fischer projection of *D*-glucose is :



- (i) Write Fischer projection for *L*-glucose.
- (ii) Give the product of reaction of *L*-glucose with Tollens' reagent.

#### OR

- (a) Name the three major classes of carbohydrates and give two examples of each of these classes.
- (b) What type of linkage is responsible for the primary structure of proteins?
- (c) Name the location where protein synthesis occurs in our body.
- (d) Explain the following terms:
  - (i) Mutarotation
- (ii) Avitaminoses

#### **SOLUTIONS**

- **Addition polymers:** Polyvinyl chloride, polythene Condensation polymers: Terylene, bakelite
- Sequence in the complementary strand: TTA AGG GCC
- Buna-N is a copolymer of 1, 3-butadiene and acrylonitrile and Buna-S is a copolymer of 1, 3-butadiene and styrene.
- 4. Invertase.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$
Glucose Fructose

- (i) Equanil is a tranquilizer. It is used for controlling depression and hypertension.
- (ii) Morphine is used as an analgesic in severe pain.
- Nucleotides are monomeric units of nucleic acids. A nucleotide is made up of sugar + heterocyclic base + phosphate group.

In case of DNA nucleotide, the sugar is D-2-deoxyribose whereas in RNA nucleotide, it is D-ribose. They also differ with respect to one base, DNA contains thymine whereas, RNA contains uracil.

Natural polymers: Those polymers which are found in plants and animals are called natural polymers e.g., proteins, starch, etc.

**Synthetic polymers:** Polymers which are prepared in laboratories are called synthetic polymers e.g., plastics (polythene), synthetic fibres (nylon 6, 6), etc.

- Tha stability of  $\alpha$ -helix structure of proteins is due to intramolecular hydrogen bonding between -NH and -CO groups of the same peptide chain. The  $\alpha$ -helix is termed as  $3.6_{13}$  helix since each turn of the helix has approximately 3.6 amino acids and hydrogen bonding leads to the formation of 13-membered ring.
- Natural sweeteners, e.g., sucrose and lactose add to calories intake and therefore many people prefer to use artificial sweeteners. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It has very sweet taste and is about 550 times more sweeter than sucrose. It is excreted from the body through urine unchanged. It appears to be entirely inert and harmless when taken. Its use is of great value to diabetic persons and people who need to control intake of calories.

Substances which are added to soap to change their properties in order to make them more useful for a particular application, are called fillers. For example,

- (i) Sodium rosinate, sodium silicate, borax and sodium carbonate are added to laundry soaps to increase their foaming ability.
- (ii) Glycerol is added to shaving soaps to prevent them from rapid drying.
- **10.** Natural rubber is *cis*-polyisoprene and is obtained by 1, 4-polymerisation of isoprene units. In rubber molecule double bonds are located between C<sub>2</sub> and C<sub>3</sub> of each isoprene unit. These cis-double bonds do not allow the polymer chains to come closer for effective interactions and hence intermolecular forces are quite weak. Thus, natural rubber i.e., cis-polyisoprene has a randomly coiled structure and hence shows elasticity.

- 11. (i) Peptide linkage: Proteins are the polymers of α-amino acids which are connected to each other by peptide bonds or peptide linkages. Chemically, peptide linkage is an amide formed between -COOH and -NH<sub>2</sub> groups by the elimination of a water molecule. Thus, peptide bond is a —CO—NH linkage e.g., when carboxyl group of glycine combines with the amino group of alanine we get a dipeptide, glycylalanine.
- (ii) Primary structure: Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific

sequence and this sequence of amino acids is said to be the primary structure of that protein. Any change in this primary structure *i.e.*, the sequence of amino acids creates a different protein.

(iii) Fibrous proteins: Fibrous proteins consist of linear thread like molecules which tend to lie side by side to form fibres. In these proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are usually insoluble in water, *e.g.*, keratin and myosin.

**12. Anionic detergent :** A detergent whose large part of the molecule is anion is called anionic detergent. These are sodium salts of sulphonated long chain alcohols or hydrocarbons e.g., sodium lauryl sulphate,  $CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$ 

**Preparation :** Alkyl hydrogen sulphate formed by treating long chain alcohols with concentrated sulphuric acid, are neutralised with alkali to form anionic detergents.

$$\begin{array}{c} \text{Conc.} \\ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{H} \\ \text{Lauryl alcohol} & \text{Lauryl hydrogen sulphate} \\ \xrightarrow{\text{NaOH}_{(aq)}} \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3^-\text{Na}^+ \\ \text{Sodium lauryl sulphate} \\ \text{(Anionic detergent)} \end{array}$$

**Uses :** These are mostly used (i) for household work (ii) in toothpastes.

13. Polymers which are degraded over a period of time by microorganism like bacteria, etc. are called biodegradable polymers. Biodegradable polymers and their degraded products do not cause any serious effect on the environment. For example, PHBV (Poly- $\beta$ -hydroxybutyrate-co- $\beta$ -hydroxyvalerate).

**14.** A unit formed by the attachment of a base to  $C_1'$  position of sugar is known as nucleoside, when nucleoside is linked to phosphoric acid at  $C_5'$  position of sugar moiety, a nucleotide is formed.

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar.

$$\begin{array}{c|c} O & & & & & & \\ \hline O - P - O - H_2C & & & & \\ \hline O - P - O - H_2C & & & \\ \hline O & & & & \\ \hline Sugar & & & \\ \hline H & & & \\ \hline H & & & \\ \hline O - P = O & & \\ \hline O & & & \\ \hline O - P = O & & \\ \hline O & & & \\ \hline Sugar & & \\ \hline H & & & \\ \hline O & & \\ \hline Sugar & & \\ \hline H & & \\ \hline O & & \\ \hline$$

The linkage resembles with two ester groups joined together. Thus, the linkage is known as diester linkage. The acid involved is phosphoric acid ( $H_3PO_4$ ).

OR

	Source	Deficiency disease
Vitamin A	Ripe yellow fruits, carrots, pumpkin, spinach, milk, fish oil	Night blindness, xerophthalmia (hardening of cornea of eye) and xerosis (drying of skin)
Vitamin E	Spinach, sweet potato, nuts and seeds	Sterility in males and miscarriage in females, mild hemolytic anaemia in newborn infants
Vitamin H	Fish, milk, banana, nuts	Dermatitis, depression and loss of hairs

**15.** (i) Semi-synthetic polymers: These are obtained from natural polymers by chemical modifications *e.g.*, cellulose derivatives as cellulose nitrate and cellulose acetate (rayon).

 $\begin{array}{c} \text{Cellulose} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{Cellulose acetate} \\ \text{Acetic anhydride} \end{array}$ 

- (ii) Cross-linked or Network polymers: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains and form a three-dimensional network structure. They are hard and rigid *e.g.*, bakelite, melamine etc.
- (iii) Fibres: These have strong intermolecular forces like hydrogen bonding or dipole-dipole interactions. They are useful in making fibres as their molecules are long and thread-like. They possess high tensile strength, high modulus and less elasticity. These strong forces also lead to close packing of chain and imparts crystalline nature *e.g.*, nylon-6,6 (polyamides), terylene (polyester), etc.
- **16.** (a) (i) Luminal: This is a sedative tranquilizer. It produces sleep and is habit forming.
- (ii) **Streptomycin**: It is an antibiotic and used to cure tuberculosis, pneumonia, etc.
- (iii) **Analgin**: It is antipyretic and analgesic. It lowers the body temperature in fever and gives relief from pain.
- **(b) Tranquilizer**: Veronal **Antibiotic**: Penicillin

Antipyretic and analgesic: Paracetamol

- 17. RNA are of three types:
- (i) Messenger RNA (*m*-RNA): It functions as a messenger carrying the information in a gene to the protein synthesising machinery.
- (ii) Transfer RNA (*t*-RNA): They transfer the amino acids from cytoplasm to the protein synthesising machinery.
- (iii) Ribosomal RNA (*r*-RNA): They associate with a set of proteins to form ribosomes. These complex structures, which physically move along an *m*-RNA molecule, catalyse the assembly of amino acids into protein chains. They also bind *t*-RNAs and various molecules necessary for protein synthesis.
- 18. (i) Glyptal: The monomers are phthalic acid,

It is used in adherent paint because it helps in fixing paints.

(ii) Nylon-6: The monomer is caprolactum.

It is used for making tyre cords because it has high tensile strength.

(iii) Neoprene: It is a polymer of chloroprene.

$$CH_2 = C - CH = CH_2$$

It is used for manufacturing conveyor belts in coal mines because it is non-flammable.

19. Some drugs do not bind to the active sites of the enzyme. These bind to a different site of enzyme which is called allosteric site. This binding of allosteric site changes the shape of the active site in such a way that substrate cannot recognise it. If the bond formed between an enzyme and an inhibitor is a strong covalent bond then the enzyme is blocked permanently.

20. 
$$OH$$

$$+ CH_2O \xrightarrow{H^+ \text{or}} OH$$

$$- CH_2OH \xrightarrow{OH^-} OH$$
Phenol -dehyde

$$H_2C$$
 $CH_2$ 
 $CH_2$ 

Novolac (*A*) is linear in structure while bakelite (*B*) is a cross linked polymer.

- **21.** (i) Sodium benzoate: food preservative; Morphine: narcotic analgesic; Equanil: tranquilizer.
- (ii) Bithional is added to soaps to reduce the odours produced by bacterial decomposition of organic matter on the skin, due to its antiseptic properties.
- (iii) Tranquilizers are used in sleeping pills because these relieve stress, reduce anxiety and fatigue by inducing sense of well-being.
- **22.** (i) **Denaturation of proteins :** Protein found in a biological system with a unique three-dimensional structure and biological activity is called native protein. When there is a physical change like change in temperature or chemical change like change in pH in the native form, the hydrogen bonds get disturbed. As a result, globules unfold and helices get uncoiled and protein loses its biological activity. This is known as denaturation of protein. During denaturation, 2° and 3° structures get destroyed but 1° structure remains intact *e.g.*, coagulation of egg while on boiling and curdling of milk.

In case of reversible denaturation process, the protein recovers its original properties and biological activity when the disruptive agent is removed. The reverse of denaturation is called renaturation.

- (ii) Amylase works in the mouth where the pH is 6.8–7.2. In the stomach pH is 1–2 thus, denaturation occurs and enzyme becomes inactive.
- 23. (i) Dettol has an antiseptic property.
- (ii) Dettol is a mixture of chloroxylenol and terpineol i.e.,

- (iii) Bithional is a compound added to soaps to impart them with antiseptic properties.
- (iv) Helpful nature, knowledge of chemistry and social welfare are the values shown by Gopal and Gaurav.
- **24.** (i) The number of moles of adenine (A) must be equal to that of thymine (T). Therefore,

$$(A + T) = 4,65,000 + 4,65,000 = 9,30,000$$

Also, 
$$\frac{A+T}{C+G} = 0.93$$
 (given)

 $\therefore$  Number of moles of (C + G)

$$=\frac{9,30,000}{0.93}=10,00,000$$

Since the number of moles of (C)

= number of moles of (G)

:. Number of moles of guanine (G)

$$=\frac{10,00,000}{2}=500,000$$

(ii) Let the percentage of  $\alpha$ -D-glucose present at equilibrium be x.

Assuming that the amount of open-chain form of glucose is negligible at equilibrium, then

Percentage of  $\beta$ -*D*-glucose at equilibrium = (100 - x)

$$\therefore \frac{x \times 112}{100} + \frac{(100 - x) \times 18.7}{100} = 52.7$$

or  $112x + 1870 - 18.7x = 52.7 \times 100$ 

or (112 - 18.7)x = 5270 - 1870

93.3 x = 3400

 $\Rightarrow x = 36.44\%$ 

.. Percentage of α-D-(+)-glucose = 36.44% and percentage of β-D-(+)-glucose = 63.56%

#### OR

(a) (i) Sucrose is dextrorotatory having  $[\alpha]_D = +66.5^\circ$ . On hydrolysis with dilute acids or enzymes, it gives equimolar D-(+)-glucose and D-(-)-fructose.

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{HCl} C_6H_{12}O_6 & + & C_6H_{12}O_6\\ \text{Sucrose} & D\text{-(+)-Glucose} & D\text{-(-)-Fructose}\\ [\alpha]_D = +52.5^\circ & [\alpha]_D = -92.4^\circ \end{array}$$

Since, D-(-)-fructose has larger specific rotation than D-(+)-glucose, the resulting mixture has specific rotation of -39.9°. Therefore, the mixture is laevorotatory.

(ii) Salt like behaviour of amino acids is due to the presence of both acidic and amino group in the same molecule. In aqueous solution, the carboxyl group loses a proton and amino group accepts a proton to form a dipolar ion or zwitter ion.

Therefore, they behave like salts rather than simple amines or carboxylic acids.

- (b) Active site of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.
- **25.** (i) 0.2% solution of phenol acts as an antiseptic while 1% solution of phenol acts as a disinfectant.
- (ii) If excess of NaHCO<sub>3</sub>, Mg(OH)<sub>2</sub> or Al(OH)<sub>3</sub> is used, it will make the stomach alkaline and trigger the production of even more HCl which may cause ulcers in the stomach. In contrast, cimetidine and ranitidine prevent the interaction of histamine with the receptor cells present in the stomach wall. This releases lesser amount of HCl.
- (iii) Antiseptics are the chemical substances which are used to either kill or prevent the growth of microorganisms. These are not harmful to living tissues and can be safely applied on wounds, cuts, diseased skin surfaces. For example, dettol, savlon, furacin, soframycin, etc.

Disinfectants are the chemical substances which kill microorganisms but they cannot be applied on living tissues. In other words, they also kill microorganisms like antiseptics but are not safe for living tissues. These are commonly applied to inanimate objects such as floor, drainage system, instruments, etc. Some common examples of disinfectants are phenol (1% solution), chlorine (0.2 to 0.4 ppm), etc.

#### OR

(i) Calcium bicarbonate makes water hard. Soap will give precipitate with this hard water and therefore, cannot be used for cleaning clothes. On the other hand, a synthetic detergent does not give precipitate in hard water because calcium ions form soluble salts that act as cleansing agent. Therefore, synthetic detergent should be used for cleaning clothes in hard water.

Name : Sodium lauryl sulphate

(b) CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>—N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Br<sup>-</sup> Hydrophobic Hydrophilic part part

Name: Cetyltrimethylammonium bromide

(c) CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub> — COO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>2</sub>CH<sub>2</sub>OH

Hydrophobic Hydrophilic

part part

Name: Polyethylene glycol stearate

26. (a) Glycine exists as zwitter ion,

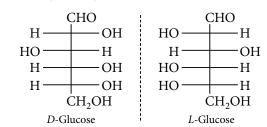
NH<sub>3</sub>—CH<sub>2</sub>—COO<sup>-</sup>. In acidic solution, it exists as cation (I), which migrates towards cathode on electrolysis.

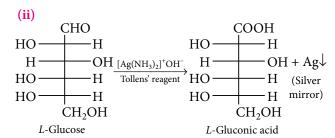
$$\begin{array}{ccc} \text{H}_{3}\overset{^{+}}{\text{N}}-\text{CH}_{2}-\text{COO}^{^{-}}+\text{H}^{^{+}} &\longrightarrow \text{H}_{3}\overset{^{+}}{\text{N}}-\text{CH}_{2}-\text{COOH} \\ & \text{Glycine} & \text{(acidic medium)} & \text{Cation I} \\ & \text{(migrates towards cathode)} \end{array}$$

In alkaline solution, glycine exists as anion (II), which on electrolysis migrates towards anode.

$$\begin{array}{ccc} \text{H}_{3}\overset{+}{\text{N}} - \text{CH}_{2} - \text{COO}^{-} + \text{OH}^{-} & \longrightarrow \text{H}_{2}\text{N} - \text{CH}_{2} - \text{COO}^{-} \\ & \text{(basic} & \text{Anion II} \\ & \text{medium)} & \text{(migrates towards anode)} \end{array}$$

**(b) (i)** The Fischer projection of *L*-glucose is the mirror image of *D*-glucose.





#### OR

- (a) (i) Monosaccharides: Glucose, fructose
- (ii) Oligosaccharides: Sucrose, raffinose
- (iii) Polysaccharides: Cellulose, starch
- (b) Peptide linkage
- (c) Ribosomes
- (d) (i) Mutarotation: The spontaneous change in specific rotation of an optically active compound with time to an equilibrium value is called mutarotation. Both forms of glucose are in equilibrium in the solution.  $\alpha$ -D-glucose  $\rightleftharpoons$  Open chain form  $\rightleftharpoons \beta$ -D-glucose

of equilibrium mixture

Sp. rotation
$$= +111^{\circ}$$
Sp. rotation
 $= +52.5^{\circ}$ 
Sp. rotation
 $= +19.2^{\circ}$ 

(ii) Avitaminoses: Multiple deficiencies caused by lack of more than one vitamin are more common in human beings. This condition of vitamin deficiency is known as avitaminoses.

MPP-8 MONTHLY Practice Problems

This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.



### Aldehydes, Ketones and Carboxylic Acids

Total Marks: 120 Time Taken: 60 Min.

#### **NEET / AIIMS**

#### **Only One Option Correct Type**

- 1. The reagent used for separation of acetaldehyde and acetophenone is
  - (a) NaHSO<sub>3</sub>
- (b)  $C_6H_5NHNH_2$
- (c) NH<sub>2</sub>OH
- (d) NaOH/I<sub>2</sub>
- **2.** When propionic acid is treated with aqueous sodium bicarbonate, CO<sub>2</sub> is liberated. The 'C' of CO<sub>2</sub> comes from
  - (a) methyl group
- (b) carboxylic acid group
- (c) methylene group
- (d) bicarbonate group.
- 3. An alkene on ozonolysis gives two moles of HCHO, one mole of CO<sub>2</sub> and one mole of CH<sub>3</sub>COCHO. What is its structure?
  - (a)  $CH_2 = C = CHCH_2CH_3$
  - (b)  $CH_2 = CHCH(CH_3)CH = CH_2$
  - (c)  $CH_2 = C = C(CH_3)_2$
  - (d)  $CH_2 = C = C(CH_3)CH = CH_2$
- **4.** A carbonyl compound with molecular weight 86, does not reduce Fehling's solution but forms crystalline bisulphite derivatives and gives iodoform test. The possible compounds can be
  - (a) 2-pentanone and 3-pentanone
  - (b) 2-pentanone and 3-methyl-2-butanone
  - (c) 2-pentanone and pentanal
  - (d) 3-pentanone and 3-methyl-2-butanone.
- **5.** Identify the main product in the given reaction.

COOH
$$(i) B_2 H_6 / ether$$

$$(ii) H_3 O^+$$

(a) 
$$CH_2CH_3$$
(b)  $CH_2OH$ 
(c)  $CH_2CH_3$ 
(d)  $CH_2CH_3$ 

- **6.** Which of the following can reduce ester to alcohol?
  - (a) NaBH<sub>4</sub>
- (b) Na/alcohol
- (c) H<sub>2</sub>/Ni
- (d) NaBH<sub>3</sub>CN
- **7.** The final product (*C*) in the given reaction is

$$\frac{\text{HCN}}{\text{pH 9-10}} (A) \xrightarrow{\text{LiAlH}_4} (B) \xrightarrow{\text{NaNO}_2} (C)$$

- 8. Which of the following does not give formaldehyde on heating or distillation?
  - (a) Formalin
- (b) Trioxane
- (c) Paraldehyde
- (d) Paraformaldehyde
- **9.** Which of the following is the correct order of  $pK_a$ values for the given compounds?  $CH_3CH_2CH(Cl)COOH(A)$ ,  $CH_3CH(Cl)CH_2COOH(B)$ ,  $CH_2ClCH_2CH_2COOH(C)$ 
  - (a) A > B > C
- (b) C > B > A
- (c) B > A > C
- (d) C > A > B
- 10. RCH<sub>2</sub>CH<sub>2</sub>OH can be converted to RCH<sub>2</sub>CH<sub>2</sub>COOH by which of the following sequence of steps?
  - (a)  $PBr_3$ , KCN,  $H_3O^+$  (b)  $PBr_3$ , KCN,  $H_2/Ni$
  - (c) KCN,  $H_3O^+$
- (d) HCN, PBr<sub>3</sub>, H<sub>3</sub>O<sup>+</sup>
- **11.** Product(*A*) formed in the given reaction

$$\begin{array}{c|c} \text{O} & \text{O} \\ \text{II} & \text{II} \\ \text{CH}_{3}\text{CCH}_{2}\text{CH}_{2}\text{COCH}_{2}\text{CH}_{3} & \xrightarrow{\text{(i) CH}_{3}\text{MgBr} \\ \text{(one mol)}} \\ \hline & \text{(ii) H}_{3}\text{O}^{+} \end{array} \Rightarrow A, \text{ is}$$

(c) 
$$H_3C$$
  $O$   $= O$ 

$$\begin{array}{c} \text{(d) } (\mathrm{CH_3})_2 \\ \mathrm{CCH_2CH_2C} \\ \mathrm{CH_3})_2 \\ \mathrm{OH} \\ \end{array}$$

12. The suitable reaction steps for the following transformation,

$$\xrightarrow{?} \xrightarrow{?} \xrightarrow{\text{Normal of } I} \text{ is }$$

(a) 
$$\xrightarrow{\text{(i) BH}_3, \text{ THF}} \xrightarrow{\text{PCC}} \xrightarrow{\text{CH}_2\text{Cl}_2}$$

(b) 
$$\xrightarrow{\text{(i) BH}_3, \text{THF}} \xrightarrow{\text{HIO}_4} \xrightarrow{\text{PIO}_4}$$

(c) 
$$\xrightarrow{\text{H}_2\text{O}, \text{H}_2\text{SO}_4 \text{ (cat.)}} \xrightarrow{\text{PCC}} \xrightarrow{\text{CH}_2\text{Cl}_2}$$

$$\text{(d)} \xrightarrow{\text{OsO}_4} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4} \xrightarrow{\text{H}_2\text{O}}$$

#### **Assertion & Reason Type**

**Directions:** In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 13. Assertion: Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

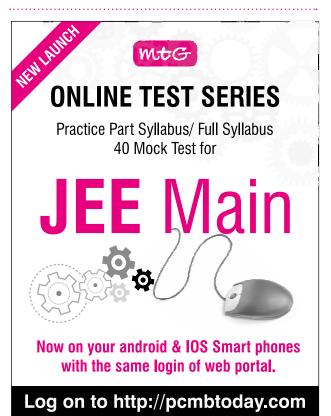
**Reason:** Aromatic aldehydes are almost as reactive as formaldehyde.

**14. Assertion**: *p*-Hydroxybenzoic acid has lower boiling point than *o*-hydroxybenzoic acid.

Reason: There exists intermolecular hydrogen bonding in o-hydroxybenzoic acid while intramolecular hydrogen bonding in *p*-hydroxybenzoic acid.

**15. Assertion**: Lower aldehydes and ketones are soluble in water but the solubility decreases as molecular mass increases.

Reason: Aldehydes and ketones can be distinguished by Tollens' test.



#### **JEE MAIN / JEE ADVANCED**

#### **Only One Option Correct Type**

- **16.** Compound 'A' (molecular formula, C<sub>3</sub>H<sub>8</sub>O) is treated with acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form a product 'B' (molecular formula, C<sub>3</sub>H<sub>6</sub>O). 'B' forms a shining silver mirror on heating with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of H<sub>2</sub>NCONHNH<sub>2</sub>.HCl and sodium acetate gives a product 'C'. Identify the structure of 'C'.
  - (a)  $CH_3CH_2CH = NNHCONH_2$
  - (b)  $(CH_3)_2C=NNHCONH_2$
  - (c)  $(CH_3)_2C=NCONHNH_2$
  - (d)  $CH_3CH_2CH = NCONHNH_2$
- 17. The one which has least iodine value is
  - (a) ginger oil
- (b) ghee
- (c) groundnut oil
- (d) sunflower oil.
- **18.** The correct set of reagents for the following conversion is

$$(CH_3)_2CHCOOH \longrightarrow \bigcirc$$

- (a)  $P/I_2$ , Na, conc.  $H_2SO_4$
- (b) P<sub>2</sub>O<sub>5</sub>, LiAlH<sub>4</sub>
- (c) P<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O, P/I<sub>2</sub>, Na
- (d) P/I<sub>2</sub>, Na, P<sub>2</sub>O<sub>5</sub>
- **19.** Which of the following has the largest value of dissociation constant  $(K_a)$ ?









#### More than One Options Correct Type

- 20. Which of the following reactions give benzophenone?
  - (a)  $2C_6H_6 + CCl_4 \xrightarrow{(i) AlCl_3} (ii) H_2O$
  - (b)  $C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3}$
  - (c) o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COC<sub>6</sub>H<sub>5</sub>  $\xrightarrow{\text{heat}}$
  - (d)  $o\text{-HOOCC}_6H_4\text{COC}_6H_5 \xrightarrow{\text{Cu}} \frac{\text{Cu}}{260^{\circ}\text{C}}$

- **21.** Which of the following are examples of aldol condensation?
  - (a)  $2CH_3CHO \xrightarrow{dil.NaOH} CH_3CHOHCH_2CHO$
  - (b)  $2CH_3COCH_3 \xrightarrow{dil.NaOH}$

CH<sub>3</sub>C(OH)(CH<sub>3</sub>)CH<sub>2</sub>COCH<sub>3</sub>

- (c)  $2HCHO \xrightarrow{dil.NaOH} CH_3OH + HCOOH$
- (d)  $C_6H_5CHO + HCHO \xrightarrow{dil.NaOH}$

 $C_6H_5CH_2OH + HCO_2Na$ 

- 22. Which of the following statements are true about C = O group?
  - (a) The carbon atom of the carbonyl group is  $sp^2$  hybridized.
  - (b) The C = O bond length is longer than that of C = C bond length.
  - (c) The portion of the molecule immediately surrounding the carbonyl group is planar.
  - (d) None of the above.
- **23.** Which of the following statements are not true about HCOOH?
  - (a) It gives CO and H<sub>2</sub>O on heating with conc. H<sub>2</sub>SO<sub>4</sub>.
  - (b) It reduces Tollens' reagent.
  - (c) It is a weaker acid than CH<sub>3</sub>COOH.
  - (d) It forms formyl chloride with PCl<sub>5</sub>.

#### **Integer Answer Type**

- **24.** A compound  $A(C_5H_8O_2)$  is reduced to pentane with Zn-Hg/HCl. It forms a dioxime with NH<sub>2</sub>OH and also gives positive iodoform and Tollens' tests. The number of ketonic groups present in A is
- **25.** Amongst the following, the number of carboxylic acids which easily undergo decarboxylation on heating are: HCOOH, (COOH)<sub>2</sub>, CH<sub>2</sub>(COOH)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>COOH, C<sub>6</sub>H<sub>5</sub>COCOOH,

#### **EXAM CORNER**

Exam	Date
JEE Main (Offline)	8 <sup>th</sup> April, 2018
WB JEE	22 <sup>nd</sup> April, 2018
JEE Advanced	20 <sup>th</sup> May, 2018
AIIMS	27 <sup>th</sup> May, 2018

26. In the given sequence of reactions, the total number of intramolecular aldol condensation products formed from 'Y' is

$$\frac{1. O_3}{2. Zn, H_2O} Y \xrightarrow{1. NaOH_{(aq)}}$$
2. Heat

#### **Comprehension Type**

An acyclic hydrocarbon P, having molecular formula C<sub>6</sub>H<sub>10</sub>, gave acetone as the only product through the following sequence of reactions, in which Q is an intermediate compound.

$$P \xrightarrow{\text{(i) dil.H}_2 \text{SO}_4/\\ \text{HgSO}_4} \xrightarrow{\text{(ii) NaBH}_4/\text{ethanol}} Q \xrightarrow{\text{(ii) conc. H}_2 \text{SO}_4\\ \text{(catalytic amount)}} 2\text{CH}_3 \text{COCH}_3$$

$$\xrightarrow{\text{(iii) O}_3} 2\text{CH}_3 \text{COCH}_3$$

- **27.** The structure of the compound *P* is
  - (a)  $CH_3CH_2CH_2CH_2C \equiv CH$
  - (b)  $CH_3CH_2C \equiv CCH_2CH_3$
  - (c)  $(CH_3)_2CHC \equiv CCH_3$
  - (d)  $(CH_3)_3CC \equiv CH$
- **28.** The structure of the compound *Q* is

(d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub>

#### Matrix Match Type

29. Match column I with column II and choose the correct option using the codes given below.

#### Column I

#### Column II

(A) 
$$CH_3$$
— $CH$ = $CH$ — $C$ — $H$ — $CH_2$ OH
$$CH_3$$
— $CH$ = $CH$ — $CH_2$ OH

(B) 
$$C_6H_5-C \equiv N \longrightarrow (q) \text{ LiAlH}$$

$$C_6H_5CHO$$

(D) 
$$C_6H_5$$
— $CH = CH$ — $C$ — $H$  (s) NaBH<sub>4</sub>

$$\longrightarrow C_6H_5CH_2CH_2CH_2OH$$

11	D	•	
(a) p	r	S	q
(b) q	S	p	r
(c) s	q	r	p
(d) s	r	p	a

30. Match column I with column II and choose the correct option using the codes given below.

(A) 
$$(COOH)_2.2H_2O \xrightarrow{\Delta} (105^{\circ}C)$$

(p) 
$$2CO_2 + H_2O$$

Column I Column II

(A) 
$$(COOH)_2.2H_2O \xrightarrow{\Delta} (p) 2CO_2 + H_2O$$

(B)  $\langle COOH \xrightarrow{P_2O_5} \Delta \rangle$  (q)  $(COOH)_2$ 

(C) 
$$(COOH)_2.2H_2O \xrightarrow{\Delta} (r)$$
 Carbon suboxic

(C) 
$$(COOH)_2.2H_2O \xrightarrow{\Delta}_{KMnO_4}$$
 (r) Carbon suboxide  
(D)  $COOH \xrightarrow{\Delta, 140-150^{\circ}C}_{COOH}$  (s)  $CH_3COOH$ 

A	В	C	D
(a) p	q	s	r
(b) r	S	q	p
(c) q	r	p	S
(d) n	а	r	c



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# **SELF CHECK**

#### Check your score! If your score is

> 90% **EXCELLENT WORK**! You are well prepared to take the challenge of final exam. 90-75% GOOD WORK! You can score good in the final exam.

No. of questions attempted No. of questions correct 74-60% SATISFACTORY! You need to score more next time.

Marks scored in percentage < 60% NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

# **EMISTRY MUSING**

**PROBLEM SET 53** 

hemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the ◆ chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

#### JEE MAIN/NEET

1. Consider the following reaction,

$$\begin{array}{c}
\text{OAc} \\
& \\
& \\
\end{array}$$

$$\begin{array}{c}
\text{RCO}_3\text{H} \\
\end{array}$$

$$X; \qquad \begin{array}{c}
\text{RCO}_3\text{H} \\
\end{array}$$

Here, X and Y respectively are

$$(a) \bigcirc O \bigcirc O (b) \bigcirc O (c) \bigcirc O (d) \bigcirc O$$

2. Consider the following set of reactions,

$$Rh + NaCl + Cl_2 \longrightarrow X$$

Na<sub>3</sub>[RhCl<sub>6</sub>].12H<sub>2</sub>O 
$$\xrightarrow{\text{Boiling with water}} Y$$
(Red coloured)

NaOH
$$Z \xrightarrow{\text{Limited amount of HCl}} [\text{RhCl}_3.3\text{H}_2\text{O}]$$
Here,  $X$ ,  $Y$  and  $Z$  are

Here, X, Y and Z are

$\boldsymbol{X}$	$\boldsymbol{Y}$	$\boldsymbol{Z}$
(a) Na[RhCl <sub>6</sub> ]	$[Rh(H_2O)_6]^{2+}$	$Rh_2O_3.H_2O$
(b) Na <sub>3</sub> [RhCl <sub>6</sub> ]	$[Rh(H_2O)_6]^{2+}$	Rh
(c) Na <sub>3</sub> [RhCl <sub>6</sub> ]	$[Rh(H_2O)_6]^{3+}$	Rh <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O

 $[Rh(H_2O)_6]^{3+}$  $[Rh(H_2O)_6]^{3+}$  $Rh_2O_3.H_2O$ (d) RhCl<sub>3</sub>

3. Observe the given sequence of reactions and choose the incorrect statement.

O  
NH-C

$$\stackrel{O}{\longrightarrow}$$
 $\stackrel{O}{\longrightarrow}$ 
 $\stackrel{Cl}{\longrightarrow}$ 
 $\stackrel{H_3O^+}{\longrightarrow}$ 
 $Q + R$ 
 $\stackrel{O}{\longrightarrow}$ 
 $\stackrel{O}{\longrightarrow}$ 

(a) 'T' is formed by coupling reaction.

(b) 'R' on heating with ammonia gives benzamide.

- (c) 'S' is a stable compound and can be isolated in solid form.
- (d) 'Q' reacts with Hinsberg's reagent to give a sulphonamide which is soluble in alkali.
- 4. Consider the following reaction,

$$KO_2 + CO_2 + H_2O \xrightarrow{\Delta} P + O_2 \uparrow$$

the correct statement about *P* is

- (a) the anion present in crystalline P exists as a dimer due to hydrogen bonding
- (b) *P* cannot be isolated in solid state
- (c) *P* is generally called potash alum
- (d) *P* gives thermally unstable carbonate on heating.
- 5. A gas is expanded from volume  $V_1$  to  $V_2$  through three different processes:
  - Reversible adiabatic
  - II. Reversible isothermal
  - III. Irreversible adiabatic (against a constant external pressure,  $P_{ex}$ )

The correct option is

(a) 
$$(T_f)_{\text{Reversible isothermal}} > (T_f)_{\text{Reversible adiabatic}}$$

 $> (T_f)_{\text{Irreversible adiabatic}}$ 

(b) 
$$(T_f)_{\text{Reversible isothermal}} > (T_f)_{\text{Irreversible adiabatic}}$$

 $> (T_f)_{\text{Reversible adiabatic}}$ 

(c) 
$$W_{\text{Reversible isothermal}} > W_{\text{Irreversible adiabatic}}$$

> W<sub>Reversible adiabatic</sub>

(d) 
$$W_{\text{Irreversible adiabatic}} > W_{\text{Reversible isothermal}}$$

 $>W_{
m Reversible\ adiabatic}$ 

#### JEE ADVANCED

- **6.** For homogenous gaseous  $X_{(g)} + 2Y_{(g)} \rightleftharpoons Z_{(g)}$  at 473 K, the value of  $K_c = 0.35$ . When 2 moles of *Y* are mixed with 1 mole of *X*, what would be the pressure when 60% of X is converted to Z?
  - (a) 200 atm
- (b) 180 atm
- (c) 400 atm
- (d) 150 atm



Dear Students! I am back again with another mind blowing question-answer series of ORGANIC CHEMISTRY. Questions are of quite standard and conceptual. Try to solve every question by yourself and then look at the solution and don't do the reverse!! Hope you will love to learn. Do take care.

\*Arunava Sarkar 💂

#### **VERY IMPORTANT PROBLEMS**

Glycerol – Identify A and B.

2. 
$$CH_3 - CH - CH - CH_3 \xrightarrow{H^+, Me_2SO}$$
?

$$\frac{\Delta}{\Delta}$$

6. 
$$\frac{\text{NaOH}}{\text{Work up}} A \xrightarrow{\text{Red P/Cl}_2} B \xrightarrow{\text{alcoholic}} KOH$$

$$? < \frac{\text{Ag}_2\text{O}/\Delta}{(2) \text{ CH}_2\text{Ng}_2}$$

Identify the final product.

#### **SOLUTIONS**

Glycerol undergoes dehydration when heated with KHSO<sub>4</sub> as follows:

$$\begin{array}{c|c} \operatorname{HO}-\operatorname{CH}_2-\operatorname{CH}-\operatorname{CH}_2 & \operatorname{KHSO}_4\\ \operatorname{OH} & \operatorname{OH} & \\ \end{array} \\ \begin{array}{c|c} \operatorname{Tautomerisation} & \operatorname{H}_2 \overset{\leftarrow}{\cap} & \operatorname{CH}_2 & \overset{\leftarrow}{\cap} & \\ \end{array} \\ \begin{array}{c|c} \operatorname{Tautomerisation} & \operatorname{H}_2 \overset{\leftarrow}{\cap} & \operatorname{CH}_2 & \overset{\leftarrow}{\cap} & \\ \end{array} \\ \operatorname{CH}_2=\operatorname{CH}-\operatorname{CH}=\operatorname{O} & \underset{\operatorname{Tischenko}}{\operatorname{Al(OEt)}_3} \\ \operatorname{Acraldehyde} & (\operatorname{Acrolein}) & \underset{\operatorname{reaction}}{\operatorname{Tischenko}} \\ \operatorname{CH}_2=\operatorname{CH}-\operatorname{C}-\operatorname{OCH}_2-\operatorname{CH}=\operatorname{CH}_2 \\ \\ \operatorname{O} \\ \end{array}$$

<sup>\*</sup>Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

$$\begin{array}{c} Cl \\ O \\ \hline CH \\ \hline \end{array} \begin{array}{c} O \\ \hline COOH \\ \hline \end{array} \begin{array}{c} O \\ \hline \end{array} \end{array} \begin{array}{c} O \\ \end{array} \end{array} \begin{array}{c} O \\ \end{array} \begin{array}{c} O \\ \end{array} \begin{array}$$

$$O = C - CH_2 - \overset{+}{N_2} \qquad O = C \xrightarrow{\overset{-}{C}H_2 - \overset{+}{N_2}} \qquad O = C \xrightarrow{\overset{-$$

7. 
$$H_3C$$
 $CH_3$ 
 $Br$ 
 $Br$ 
 $Br$ 
 $Br$ 
 $Br$ 
 $CH_3$ 
 $CH$ 

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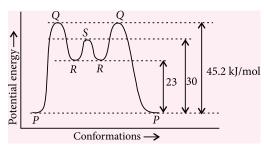
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# lanced

#### SECTION-1 (MAXIMUM MARKS : 40)

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which one or more than one answer is correct. For each question you will be awarded 4 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marking in this section.

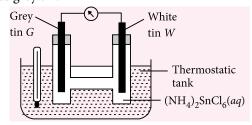
- 1. Which of the following statements regarding a peptide linkage in a protein molecule is/are correct?
  - (a) It is an amide linkage.
  - (b) It has partial double bond character.
  - (c) It is hydrophilic in nature.
  - (d) It connects protein molecules through H-bonds.
- 2. Under Wolff-Kishner reduction conditions, the conversions which may be brought about are
  - (a) benzophenone into diphenylmethane
  - (b) benzaldehyde into benzyl alcohol
  - (c) cyclohexanone into cyclohexane
  - (d) cyclohexanone into cyclohexanol.
- 3. Metallurgies of which of the following metals involve(s) leaching?
  - (a) Au
- (b) Ag
- (c) Al
- (d) Fe
- **4.** Find the correct statement(s).
  - (a) Schottky defect is also called dislocation defect.
  - (b) Unit cell having crystal parameters,  $a = b \neq c$ ,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 120^{\circ}$  is hexagonal.
  - (c) In ionic compounds having Frenkel defect, the ratio  $r^+/r^-$  is high.
  - (d) The coordination number of Na<sup>+</sup> ion in NaCl is 8.
- 5. For cyclohexane, four types of conformations have been found. These are chair, half chair, twist boat and boat form. Energy diagram of different conformers of cyclohexane is given. Choose the correct option(s).



- (a) Point *R* corresponds to chair form.
- (b) Point S corresponds to chair form.
- (c) Point Q corresponds to boat form.
- (d) None of these.
- During one of his adventures Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous and contains CO in addition to O<sub>2</sub> and N<sub>2</sub>. Sabu, being huge, could not enter cave. In order to save Chacha Chaudhary he started sucking the poisonous air out of the cave by mouth. In each cycle he used to fill his lungs with cave air and exhale it out in the surroundings. In the mean time fresh air  $(N_2 + O_2)$  from the surrounding effused into cave till the pressure was 1 atmosphere. Each time Sabu sucked air, the pressure in the cave dropped to 1/2 atm. An initial sample of air taken from the cave measured 11.2 mL at STP and give 7 J on complete combustion at constant pressure.
  - (i) If the safe level of CO required in cave for life is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary.
  - (ii) Sabu should rescue Chacha Chaudhary within 10 minutes else he will die. Precious 80 s was wasted in thinking of a way to rescue him. At maximum how much time should each cycle of inhaling and exhaling take?

[Given :  $\Delta H_{\text{comb}}CO = -280 \text{ kJ mol}^{-1}$ . Neglect Graham's law effect during operations.]

- (a) 8 times
- (b) 13 times
- (c) 40 s
- (d) 20 s
- 7. The diagram shows an apparatus to find the transition temperature (18 °C) at which white tin and grey tin are in equilibrium. Below 18 °C, white tin dissolves from W and is deposited on G as grey tin.

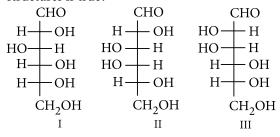


Which of the following statements are correct?

- (a) The stable form of tin at 25 °C is grey.
- (b) Below 18°C, electrons flow through the external circuit from W to G.
- (c) At 18 °C, no current flows.
- (d) At 25 °C, current flows from W to G.
- 8. The gas phase decomposition of dimethyl ether follows first order kinetics,

 $CH_3$ —O— $CH_{3(g)}$   $\longrightarrow$   $CH_{4(g)} + H_{2(g)} + CO_{(g)}$ The reaction is carried out in a constant volume container at 500 °C and has a half life of 0.116 hours. Initially only dimethyl ether is present at a pressure of 10 atm. (Assume ideal gas behaviour.)

- (a) The total pressure of the system after 23.03 min is 9 atm.
- (b) The total pressure of the system after 23.03 min is 28 atm.
- (c) The partial pressure of dimethyl ether after 23.03 min is 1 atm.
- (d) The partial pressure of methane after 23.03 min is 9 atm.
- 9. Which of the statements regarding following structures is true?



- (a) I and II are epimers.
- (b) I and III are epimers.
- (c) I and II are enantiomers.
- (d) I and III are enantiomers.

- **10.** Choose the correct characteristic test(s) of anions.
  - (a) Sulphide: With dilute H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>S is evolved which turns lead acetate paper black and with sodium nitroprusside, sulphide gives purple

$$Pb(CH_3COO)_2 + H_2S \rightarrow PbS + 2CH_3COOH$$
(black)

$$Na_2[Fe(CN)_5NO] + Na_2S \rightarrow Na_4[Fe(CN)_5NOS]$$
(purple)

(b) Sulphite: With dilute H<sub>2</sub>SO<sub>4</sub>, SO<sub>2</sub> is released which turns potassium dichromate paper green.

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

- (c) Nitrite: With dilute H<sub>2</sub>SO<sub>4</sub>, nitric oxide is released which combines with atmospheric oxygen to give reddish-brown fumes. The nitric oxide turns ferrous sulphate solution brownishblack (FeSO<sub>4</sub> · NO).
- (d) Chlorides: With concentrated H<sub>2</sub>SO<sub>4</sub>, HCl gas is released which gives white fumes with ammonia. Silver nitrate solution gives white precipitate with Cl<sup>-</sup> which is soluble in ammonia.

$$Cl^- + Ag^+ \rightarrow AgCl \downarrow$$

$$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

The characteristic test of Cl<sup>-</sup> is chromyl chloride

$$K_2Cr_2O_7 + 4Cl^- + 6H_2SO_4 \rightarrow$$
 $2CrO_2Cl_2 + 2KHSO_4 + 4HSO_4^- + 3H_2O$ 
(red vapours)

$$\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \rightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$$
(Yellow soln.)

$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow$$

#### SECTION-2 (MAXIMUM MARKS: 40)

This section contains 10 integer type questions. Answers are to be given in between 0 to 9 in the form of nearest integer. Each question carries 4 marks if you darken the correct answer and no negative mark will be awarded for an incorrectly bubbled answer.

- 11. When C<sub>2</sub>H<sub>5</sub>COONa is electrolysed, the main organic compound formed is  $C_pH_qO_r$ . Then integer value of 'r' is
- 12. How many of the following sulphides salts are black in colour? CdS, ZnS, NiS, PbS, CuS, Bi<sub>2</sub>S<sub>3</sub>
- **13.** A certain gas diffuses from two different vessels *P* and Q. The vessel P has a circular orifice while vessel Q has square orifice of length equal to the radius

of the orifice of vessel P. The rates of diffusion of the gas from vessel P to vessel Q under similar temperature and pressure condition is

- 14. 1 g sample of pure organic compound containing chlorine is fused with Na<sub>2</sub>O<sub>2</sub> to convert chlorine to NaCl. The sample is then dissolved in water and the chloride precipitated with AgNO<sub>3</sub>, giving 1.96 g of AgCl. If the molecular weight of organic compound is 147, how many chlorine atoms does each molecule contain?
- **15.** Amongst the following, the total number of compounds which are soluble in aqueous NaOH is

- **16.** Read the following statements from 0 to 9 and choose the incorrect statement.
  - 0. Both glucose and fructose give positive test with Tollens' reagent.

gives positive test with Tollens' reagent.

- 2. Thermosetting polymers are the polymers which undergo permanent change on heating.
- 3. A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc. is called condensation polymer.
- 4. Buna-S is obtained by polymerization of

- 1,3-butadiene and styrene in the ratio of 3 : 1 in presence of sodium.
- 5. Natural rubber is a polymer of chloroprene.
- 6. Glycine gives purple colour with ninhydrin while acetamide does not.
- 7. Raffinose is a trisaccharide and on hydrolysis it gives three molecules of monosaccharide units one each of glucose, fructose and galactose.
- According to Maxwell distribution law, at high temperatures a greater fraction of the molecules can be expected to have high speed than at low temperatures.
- 9. The entropy of a perfectly ordered crystalline substance at 0 K is zero.

17. 
$$\frac{1}{1}$$
 Br  $\frac{\text{NaNH}_2}{\text{NH}_3}$  Major product

In the substitution product,  $-NH_2$  group is present at C—position.

- **18.** The vapour pressure of pure liquid A is 0.80 atm. When a non-volatile liquid B is added to A its vapour pressure drops to 0.60 atm. The mole fraction of B in the solution is 1/x. Find the value of x.
- **19.** In antifluorite structure coordination number of anion is \_\_\_\_.
- **20.** 3 moles of acetone when heated with dry HCl gives phoron. How many  $sp^2$  hybridised carbon atoms are present in phoron?

			WIASAAFI	, ,,,			
1.	(a,b,c,d)	2.	(a,c)	3.	(a,b,c)	4.	(b)
<b>5.</b>	(d)	6.	(b,c)	7.	(b,c,d)		
8.	(b,c,d)	9.	(a,b)	10.	(a,b,c,d)	11.	(0)
12.	(4)	13.	(3)	14.	(2)	15.	(7)
<b>16.</b>	(5)	17.	(3)	18.	(4)	19.	(8)
20.	(5)						

For detailed solution to JEE Advanced Practice Problems, visit our website : www.vidyalankar.org

#### **Solution Senders of Chemistry Musing**

Set - 52

- Subhankar Panda, West Bengal
- Raghav Malhotra, Maharashtra

Set - 51

Anshuman Pan, West Bengal

### **CHEMISTRY MUSING**

#### **SOLUTION SET 52**

1. (d): Molar volume from pyknometric density

$$= \frac{\text{Weight or mass}}{\text{Density}} = \frac{\text{Weight } (w)}{2.165 \times 10^3} \text{ m}^3$$
Molar volume from X-ray density = 
$$\frac{w}{2.178 \times 10^3} \text{ m}^3$$

Volume unoccupied = 
$$\frac{w}{10^3} \left( \frac{1}{2.165} - \frac{1}{2.178} \right) \text{m}^3$$
  
=  $\frac{0.013 \text{ w} \times 10^{-3}}{2.165 \times 2.178}$ 

:. Fraction unoccupied

$$= \frac{\left(\frac{0.013 \text{ w} \times 10^{-3}}{2.165 \times 2.178}\right)}{\left(\frac{\text{w} \times 10^{-3}}{2.165}\right)} = 5.96 \times 10^{-3}$$

2. (a): 
$$4B + 3O_2 \xrightarrow{700 \text{ °C}} 2B_2O_3$$
  
 $2B + N_2 \xrightarrow{\text{high}} 2BN$ 

A'

B'

(white amorphous powder)

$$BN + 3H_2O \xrightarrow{\Delta} H_3BO_3 + NH_{3(g)}$$

$$C \quad D'$$
(white powder)

'D' turns red litmus blue because it is basic in nature and gives brown ppt. with K<sub>2</sub>HgI<sub>4</sub>.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow NH_2 - Hg - O - Hg - I$$
Brown ppt.

Its aqueous solution gives reddish brown ppt. with Nessler reagent, K<sub>2</sub>HgI<sub>4</sub>.

Nessler reagent, 
$$K_2HgI_4$$
.  
 $2H_3BO_3 \xrightarrow{heat} B_2O_3 + 3H_2O$   
 $C'$   $E'$ 

3. (b): Leaching of Carnotite,

$$K_2(UO_2)_2(VO_4)_2.3H_2O + 6CO_3^2 \longrightarrow 2K^+ + 2[UO_2(CO_3)_3]^4$$
Carnotite

 $Uranyl \ carbonate$ 
 $+ 2VO_3^- + 4OH^- + H_2O$ 
 $2[UO_2(CO_3)_3]^{4-} + 6OH^- + 2Na^+ \longrightarrow Na_2U_3O_7 + 6CO_3^2$ 
 $+ 3H_2O$ 

**4.** (d): Reaction  $T_2O_3 \longrightarrow T$  is possible above that temperature where line of T crosses the line of R.

5. (c): LiCl.3NH<sub>3(s)</sub> 
$$\Longrightarrow$$
 LiCl.NH<sub>3(s)</sub> + 2NH<sub>3(g)</sub>  $K_p = 9 \text{ atm}^2$ 

LiCl.NH<sub>3(s)</sub> + 2NH<sub>3(g)</sub> 
$$\rightleftharpoons$$
 LiCl.3NH<sub>3(s)</sub>  
 $t = 0$  0.1  $a$  0  
 $t = t_{eq}$  0  $(a - 0.2)$  0.1

Initially *a* moles of NH<sub>3</sub> should be added to bring in completion of reaction.

$$K_{p_1} = \frac{1}{(p'_{\text{NH}_3})^2} \Rightarrow \frac{1}{9} = \frac{1}{(p'_{\text{NH}_3})^2}$$
  
 $\Rightarrow p'_{\text{NH}_3} = 3 \text{ atm}$   
 $PV = nRT$   
 $3 \times 5 = n \times 0.0821 \times 313$   
 $n = 0.5837$   
 $(a - 0.2) = 0.5837$ 

Mole of  $NH_3 = a = 0.5837 + 0.2$ 

= 0.7837 mole of NH<sub>3</sub> should be added for completion of reaction.

**6. (c)**: In case of octahedral complexes of  $d^4$  ions when  $\Delta_o > P$ , low spin complexes are formed and when  $\Delta_o < P$ , high spin complexes are formed. In case of octahedral complexes of  $d^9$  ions in both cases the number of unpaired electrons is same.

(i) For  $d^9$  complex

Distribution of  $d^9$  electrons in  $t_{2g}$  and  $e_g$  orbitals

(ii) For  $d^4$  complex,

$$e_{g}^{0} - - \cdots - e_{g}^{1}$$

$$t_{2g}^{4} \uparrow \downarrow \uparrow \uparrow \cdots - d^{4} \text{ ion } \cdots - f - e_{g}^{1}$$

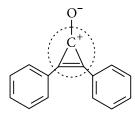
$$\Delta_{o} > P \text{ (LS complex)}$$

$$(n = 2) \qquad \Delta_{o} < P \text{ (HS complex)}$$

$$(n = 4)$$

Distribution of  $d^4$  electrons in  $t_{2\sigma}$  and  $e_{\sigma}$  orbitals

7. **(b)**: The structure given in option (b) contributes heavily to the dipole moment as it shows greater aromatic character than others.



**8. (d):** The all *cis*-isomer (a), a fully convex decagon, would have angles of 144° which creates large amount of angle strain.

The all cis-isomer can adopt boat like conformation.

(c) to relieve the angle strain but it is still unstable as compared to *trans*, *cis*, *trans*, *cis*, *cis* isomer (b). (b) is unstable due to steric repulsion between two internal hydrogens.

The non-planar *trans*, *cis*, *cis*, *cis*, *cis* isomer (d) is the most stable of all the possible isomers.

- **9. (4):** If the isoelectric point (pI) of a polypeptide is more than 7, then it will exist as positively charged at pH = 7. This is possible only if the polypeptide is basic in nature, *i.e.*, it has two or more amino groups. In other words, side chain  $R_1$  and  $R_2$  must contain —NH<sub>2</sub> groups but not —CONH<sub>2</sub> groups which are almost neutral. So, polypeptides (IV), (VI), (VIII) and (IX) will be positively charged at pH = 7, *i.e.*, the correct integer is A
- 10. (2): The equations required are  $H_2O + 2KI + O_3 \longrightarrow I_2 + O_2 + 2KOH$   $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

Milliequivalents of iodine = Milliequivalents of KI = Milliequivalents of  $O_3$  reacted = 2 × Milliequivalents of hypo

Milliequivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> =  $1.5 \times 0.01 = 1.5 \times 10^{-2}$ 

Millimoles of iodine = 
$$\frac{1.5 \times 10^{-2}}{2} = 7.5 \times 10^{-3}$$

[: 'n' factor for iodine = 2]

Millimoles of ozone =  $7.5 \times 10^{-3}$ 

Volume of ozone = 
$$\frac{nRT}{P} = \frac{7.5 \times 10^{-6} \times 0.0821 \times 300}{1}$$
  
=  $184.725 \times 10^{-6}$  L

Volume percentage of ozone = 
$$\frac{184.725 \times 10^{-6}}{9} \times 100$$
$$= 2.05 \times 10^{-3}$$

Thus, x is 2.



Contd. from page no. 82

#### **CHEMISTRY MUSING**



#### COMPREHENSION

A mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing (A), when heated with alcoholic solution of KOH produce  $C_7H_5N$  (C) associated with unpleasant odour.

- **7.** What is *A*?
  - (a)  $C_6H_5NH_2$
- (b)  $C_6H_5CH_3$
- (c) C<sub>6</sub>H<sub>5</sub>CHO
- (d) None of these
- 8. The alkaline aqueous layer (B) when heated with chloroform and then acidified give a mixture of isomeric compounds of molecular formula C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>.
  (B) is
  - (a) C<sub>6</sub>H<sub>5</sub>CHO
- (b) C<sub>6</sub>H<sub>5</sub>COOH
- (c)  $C_6H_5CH_3$
- (d) none of these.

#### INTEGER VALUE

9. When a certain metal was irradiated with light of frequency  $4.0 \times 10^{16} \, \text{s}^{-1}$ , the photoelectrons emitted has three times the kinetic energy as the kinetic energy of photoelectrons emitted when the metal was irradiated with light of frequency  $2.0 \times 10^{16} \, \text{s}^{-1}$ .

The critical frequency ( $v_0$ ) of the metal calculated is  $x \times 10^{16}$  s<sup>-1</sup>. Then, the value of x is

10. The resistance of N/10 solution is found to be  $2.5 \times 10^3$  ohms. The equivalent conductance of the solution is (cell constant = 1.25 cm<sup>-1</sup>)



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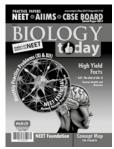


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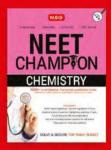
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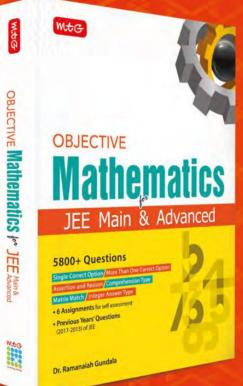




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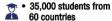
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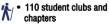


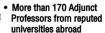
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